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FORMATION AND REDUCTION OF POLYCHLORINATED DIBENZO-*P*-DIOXINS/DIBENZOFURANS IN FLUIDIZED BED COMBUSTION OF SOLID WASTE

Master of Science Thesis

Examiner: Professor Antti Oksanen
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ABSTRACT

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Polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) are proven to possess high biological toxicity. They are formed in large quantities in industrial waste combustion processes. The formation of PCDD/F in grate-fired municipal waste incinerators (MWI) is widely investigated unlike the formation in fluidized bed (FB) boilers.

This work aims to define the key differences in the formation of PCDD/Fs between grate-fired and FB boilers using solid waste as fuel. The theoretical part of the work involves a comprehensive review of the formation and reduction of PCDD/Fs in waste combustion. The experimental part consists of participating in two PCDD/F measurement campaigns at FB boiler plants and the analysis of the results.

The main PCDD/F formation routes in thermal processes include the high temperature gas phase formation from precursors (pyrosynthesis), the condensation of precursors on surfaces of metal catalysts (precursor mechanism), and the formation from residual carbon in the fly ash in presence of a catalyst (de novo synthesis). Two latter pathways take place in post-combustion zone at temperatures from 200 to 500 ºC and they are suggested to be mainly responsible of the overall PCDD/F formation.

The key factors promoting the formation of PCDD/Fs include incomplete combustion of the fuel, oxidizing atmosphere, presence of chlorine, residual carbon in the fly ash, favorable temperature window, and copper catalyst. Copper (chloride) is found to highly enhance the formation of PCDD/Fs. The change in different forms of copper is found to depend on temperature, which could partly explain the 'temperature window' of PCDD/F formation. Therefore, the flue gas residence time in this region should be minimized.

Sulfur-, nitrogen-, and calcium-based compounds are found to inhibit the formation of PCDD/Fs. SO_2 in the flue gas may participate in the formation of metal sulfates from copper chlorides, thus reducing the active sites of the copper catalysts. Addition of CaO or $CaCO_3$ into the flue gases may reduce PCDD/Fs due to their capability to adsorb PCDD/Fs or by changing the pH of the fly ash towards the alkaline side.

Flue gas cleaning devices, especially electrostatic precipitators (ESP), may offer a favorable framework for PCDD/F formation if operated at temperatures above 200 ºC. Bag house filters with prior injection of additives can effectively reduce PCDD/F emissions (up to 99.5%). Catalytic decomposition of PCDD/Fs is the only method that will destroy the PCDD/Fs, not only transfer the problem elsewhere.

The PCDD/F congener patterns (fingerprints) from grate-fired boilers and FB boilers possess great similarity, thus the governing formation routes are similar in both cases. The main factors causing dissimilarities in the fingerprints involve fuel properties (amount of copper and chlorine) and fly ash characteristics that are influenced by the combustion technology and feeding of additives. Differences in the gas/solid partitioning between different technologies are suggested to mainly depend on the fly ash characteristics, and differences in the sampling temperatures and methods.

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Polykloorattujen dibenzo-*p*-dioksiinien/dibenzofuraanien (PCDD/F) on todistettu olevan biologisesti erittäin myrkyllisiä. Niitä syntyy suuria määriä teollisissa jätteenpolttoprosesseissa. PCDD/F-yhdisteiden muodostumista jätteen arinapoltossa on tutkittu laajasti toisin kuin niiden muodostumista leijupoltossa.

Tämän työn tavoiteena on määrittää merkittävimmät erot PCDD/F-yhdisteiden syntymisessä kiinteän jätteen arina- ja leijupolton välillä. Työn teoriaosuus koostuu kattavasta kirjallisuusselvityksestä PCDD/F-yhdisteiden muodostumisesta ja vähenemisestä jätteenpoltossa. Työn kokeellinen osuus pitää sisällään osallistumisen kahteen PCDD/F-mittauskampanjaan leijukattilalaitoksilla, sekä mittausten tuloksien analysoinnin.

Tärkeimmät PCDD/F-muodostumisreitit lämpöprosesseissa ovat korkean lämpötilan kaasufaasimuodostuminen (pyrosynteesi), PCDD/F-esiyhdisteiden kondensaatio metallikatalyytin pinnalla, sekä muodostuminen lentotuhkan jäännöshiilestä katalyytin läsnäollessa. Kaksi jälkimmäistä muodostumisreittiä tapahtuvat kattilan jälkeisissä savukaasukanavissa 200-500 ºC lämpötilassa ja niiden on havaittu olevan pääasiallisesti vastuussa PCDD/F-yhdisteiden muodostumisesta.

Tärkeimmät PCDD/F-yhdisteiden muodostumista edistävät tekijät ovat polttoaineen epätäydellinen palaminen, hapettavat olosuhteet, kloorin läsnäolo, lentotuhkan jäännöshiili, toivottu lämpötila-alue, sekä kuparikatalyytti. Kupari(kloridin) on havaittu edistävän PCDD/F-yhdisteiden muodostumista. Eri kupariyhdisteiden osuuksien on havaittu riippuvan lämpötilasta, mikä voi osaltaan selittää PCDD/F-muodostumisen ’lämpötilaikkunan’. Savukaasun viipymäaika tällä alueella tulisi minimoida.

Rikki-, typpi- ja kalsiumyhdisteiden on havaittu vähentävän PCDD/F-yhdisteiden muodostumista. Savukaasun SO_2 voi osallistua metallisulfaattien muodostumiseen metalliklorideista, mikä vähentää kuparikatalyytin aktiivisuutta. CaO tai $CaCO_3$ lisääminen savukaasuun voi vähentää PCDD/F-yhdisteitä niiden hyvän adsorptiokyvyn, sekä lisäyksestä aiheutuvan lentotuhkan pH-arvon nousun takia.

Savukaasunpuhdistuslaitteet, erityisesti sähkösuodin, voivat toimia otollisena ympäristönä PCDD/F:n muodostumiselle jos niitä käytetään yli 200 ºC:ssa. Letkusuotimilla ja lisäaineiden syötöllä voidaan puhdistaa tehokkaasti PCDD/F-yhdisteitä (99.5%). PCDD/F:n katalyyttinen hajotus on ainoa keino, jolla ne saadaan tuhottua kokonaan eikä vain siirrettyä ongelmaa muualle.

PCDD/F-kongeneerijakaumat (sormenjäljet) arinakattiloista ja leijukattiloista ovat hyvin samanlaisia, mikä osoittaa, että vallitsevat muodostumisreitit ovat samat molemmissa tapauksissa. Erot PCDD/F-jakaumissa aiheutuvat eroista sekä polttoaineen, että lentotuhkan ominaisuuksissa. Lentotuhkan ominaisuuksiin vaikuttavat käytettävä polttoteknologia sekä lisäaineiden syöttö. Havaitut erot kaasu/kiinteä -jakautumisessa eri kattiloiden välillä oletetaan aiheutuvan sekä eroista lentotuhkan ominaisuuksissa eri polttotekniikoiden välillä, että eroista mittauslämpötiloissa ja –menetelmissä.

PREFACE

This thesis work was part of research work in Metso Power Oy and it was written between November 2012 and June 2013. In summer 2012, I started working at Metso Power as a summer trainee doing a literature review of dioxins emissions from waste combustion. As a natural follow-on, we decided to deepen our understanding of the topic by means of this thesis work, in which the dioxin emissions from different combustion processes are discussed in more detail and the most recent measurement data from the measurement campaigns is analyzed. During the project, I gained a lot of experience on different processes and equipment related to fluidized bed combustion, waste combustion, flue gas cleaning and flue gas emissions in general. The professional highlight of the year 2013 was participating in the 10-day measurement campaign at Metso Power's boiler plant.

First of all, I would like to thank Metso Power for giving me the possibility to participate in the interesting and challenging research projects. My sincere gratitude belongs to Satu Similä and Mikko Anttila for giving me the best possible information, support and resources to complete this work and to Merja Hedman, Katriina Jalkanen, Maaret Karppinen, and Margareta Lundberg for their guidance during the long project. I am grateful to all other co-workers at Metso Power, Umeå University, Force Technology Sweden AB and Tauw and to my professor Antti Oksanen for supervising this thesis work. Finally, I would thank to my family and friends for their support and understanding during my studies at Tampere University of Technology. Studying at TUT has honestly been the best time of my life.

Tampere, 15 September 2013

Juha Jokiluoma

Contents

TERMS AND ABBREVIATIONS

T-	Tri
Te-	Tetra
Pe-	Penta
Hx-	Hexa
Hp-	Hepta
O-	Octa
P-	Poly
C-	Chlorinated or chloro-
AC	Activated carbon
Bz	Benzene
BFB	Bubbling Fluidized Bed
BHF	Bag House Filter
Carbon matrix	Residual carbon with a complex geometrical structure
Carcinogenic	Compound that causes cancer
CFB	Circulating Fluidized Bed
Congener	A compound of same characteristic or category as another
Cupric	Copper species of two oxidation states
Cuprous	Copper species of one oxidation state
Cyclization	Formation of aromatic hydrocarbons
DD	Dibenzo-*p*-dioxin
DF	Dibenzofuran
De novo synthesis	PCDD/F formation from carbon matrices (residual carbon) through a series of chlorination and oxidation reactions
Dimerization	Formation of dimer (compound consisting of two aromatic rings) of two monomers (compounds of one aromatic ring)
Eco	Economizer; Feed water pre-heater
Electrophilic substitution	Substitution of an electrophile (H) by a functional group or atom (Cl). A typical reaction for aromatic compounds.
ESP	Electrostatic Precipitator
FB	Fluidized Bed
Heterogeneous formation	Formation with presence of a catalyst
Homogeneous formation	Formation without presence of a catalyst
Homologue	A group of isomers (PCDDs or PCDFs with same amount of chlorine atoms attached to the aromatic rings)
IE-directive	Directive 2010/75/EU of European Parliament and the Council of 24 November 2010 on Industrial Emissions
Isomer	A compound of same molecular formula but different arrangement of atoms

I-TEF	International Toxicity Equivalent Factors
I-TEQ	International Toxic Equivalent
Luvo	Combustion air pre-heater
MSWI	Municipal solid waste incinerator
MSW	Municipal solid waste
MWI	Municipal waste incinerator (grate-fired)
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCBz	Polychlorinated benzene
PCDD	Polychlorinated dibenzo-*p*-dioxin
PCDF	Polychlorinated dibenzofuran
PCPh	Polychlorinated phenol
Ph	Phenol
PIC	Product of incomplete combustion
POP	Persistent organic pollutants
Pyrosynthesis	PCDD/F formation in the gas phase at high temperatures
TEF	Toxicity Equivalent Factor
TEQ	Toxic Equivalent
WHO-TEF_{98}	Toxic Equivalent Factors recommended by World Health Organization. The recommendation was introduced in 1998.

1 INTRODUCTION

This thesis work was composed as part of research work on waste combustion in Metso Power, which is a part of Metso Corporation. Metso is a global supplier of technology and services to customers in the process industries, including mining, construction, pulp and paper, power, and oil and gas. Metso's pulp, paper and power professionals specialize in processes, machinery, equipment, services, paper machine clothing and filter fabrics. The core products of Metso Power include fluidized bed boilers, recovery boilers, and gasification plants. Waste combustion is a sustainable method for producing energy from waste. However, thermal treatment of waste always involves high risks of generation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), which are found to possess high biological toxicity.

The aim of this thesis work is to determine the major differences in the formation of PCDD/Fs between grate-fired and fluidized bed (FB) boilers using solid waste as fuel. The work consists of theoretical and experimental parts. The theoretical part includes a review of the main PCDD/F formation routes, the role of combustion conditions and key parameters in PCDD/F formation, the effect of flue gas cleaning on PCDD/F emissions. In addition, PCDD/F congener distributions (fingerprints) will be analyzed. The experimental part of the work involves participation in PCDD/F measurement campaigns at two FB boiler plants. The target of the measurement campaigns was to determine the performance of flue gas cleaning and behavior of PCDD/Fs. The main results of the PCDD/F measurements will be analyzed in order to define the governing PCDD/F formation routes and key parameters in the formation of PCDD/Fs in those boiler plants.

Municipal and industrial wastes have been widely used as a fuel in industrial power plants for over a century. In 1977, PCDD/Fs were found in the fly ashes and flue gases of municipal waste incinerators (Olie K. et al. 1977). Since then, the formation of PCDD/Fs in waste incineration has been widely investigated and the governing formation routes are well understood (Tuppurainen K. et al. 1998). Most of the reports, however, are concentrated in PCDD/F formation in grate-fired boilers and only minor amount of information of waste combustion in fluidized bed boilers is available. This work was composed in order to offer more information of PCDD/F formation in fluidized bed boilers.

Due to relatively large amounts of chlorine and copper (Tuppurainen K. et al. 1998, p. 2) found in waste fuels, high amounts of PCDD/Fs are produced in waste combustion processes. Because of the high toxicity of PCDD/Fs, in Europe the limit values are set as low as 0.1 ng/m^{3}n (I-TEQ, dry gas, 11%-O_2) (D 2010/75/EU, p. 69). This emission

limit can be reached by effective cleaning of the flue gases and stricter emission limits will be expected in the future. In order to reach the PCDD/F emission limits, it is essential to understand the fundamentals of PCDD/F formation, destruction, and reduction in waste combustion processes.

PCDD/F fingerprints can be used as a tool for defining the dominating formation pathways (Ryu J.-Y. et al. 2006). In industrial boiler plants, however, only a group of 17 PCDD/F congeners of the possible 210 congeners are measured due to their toxic characteristic. Therefore, the evaluation of the results from the measurement campaigns is possible only to a certain extent. The measurement and sampling of PCDD/Fs at higher temperatures are also challenging and several factors may have negative influence on the results. These topics will be discussed in detail in this thesis work.

2 BACKGROUND

2.1 A brief history of waste incineration

The first waste incineration plant was constructed in 1874 in Nottingham, England. At that time, the amount of household waste was growing and there was lack of free space for waste landfill. The main purpose of waste incineration was to destroy the waste, and that is why in England the incinerators were called as 'destructors'. This was also a method for fighting against general diseases and epidemics, such as cholera, which killed over 250 000 people in London between 1848 and 1852. (Herbert L. 2007, p. 10-16)

In Europe, the use of waste for energy production started in the early 20th century, when the first district heating plants using waste as fuel were constructed. This occurred in the areas where district heating grids already existed, mainly in Scandinavia. (Kleis H. & Dalager S. 2007, p. 6-17) At the time, the character of waste incineration business was different, as the waste was collected by horse carts and the waste was separated by human hands. (Herbert L. 2007, p. 22)

The oil crisis in the 1970's initiated a revolution in energy production. As the oil price increased, alternative energy sources had to be considered. This led to an increase in waste incineration. (Ecoprog 2012, p. 56) In addition, utilization of new technologies for waste incineration, such as fluidized bed combustion, began. In 1977, dioxins and furans were found for the first time in municipal waste incinerator fly ashes by Olie Kees. (Olie K. et al. 1997, p. 2) This started a long debate against the toxic emissions from waste incineration.

In the 1980's, the public interest towards the emissions from waste combustion increased. More attention was paid to flue gas cleaning and the discussion of air pollution started to be more active. New national and international legislations were created, which resulted in extinction of smaller waste incinerators which were not equipped with adequate emission control systems. Still, waste incineration was rather a way to reduce waste, than a business. (Ecoprog 2012, p. 56; Kleis H. & Dalager S. 2007, p.32)

In the 1990's, the utilization of waste in combined heat and power (CHP) production became more common and it is the main waste incineration method nowadays. Most of the waste incinerators today are grate boilers, which have maintained their position in the market due to competitive investment costs and simple or non-existent need for raw material pretreatment. Another widely used waste combustion technology is fluidized bed combustion, which is today one of the core businesses of Metso Power. Fluidized bed (FB) boilers are often used in co-firing of different materials, which allows

combustion of waste together with other fuels, such as coal or peat. Metso Power has long history in waste combustion business including deliveries and retrofits of over ten circulating fluidized bed (CFB) and over twenty bubbling fluidized bed (BFB) boilers combusting waste fuels (demolition wood, municipal solid waste, industrial waste). About half of them use only waste fractions as fuel, and the other half are co-combustion plants. The development of new technologies for waste-to-energy business is currently in progress. One example of modern-day technologies is the gasification of municipal waste, which was successfully introduced at Lahti Energia's power plant in Finland, in 2012. The plant is delivered by Metso Power.

2.2 Dioxins in the environment

Nowadays, dioxins and furans are mostly discussed in the context of waste incineration. However, they have also become infamous for other reasons. Agent Orange was a chemical dioxin-based weapon that was sprayed over large areas of Vietnamese countryside by U.S. army during the Vietnam War. Millions of people were exposed to dioxin, more precisely to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TeCDD), that is one of the most toxic compounds ever known. Therefore, thousands of children were born disabled and considerable number of older people suffers from cancer and other diseases. The Red Cross of Vietnam estimates that over one million people have disabilities due to the 'Agent Orange'. (IFRC 2012)

One of the most severe environmental disasters in human history was the Seveso disaster. A chemical plant producing trichlorophenol (TCP), which is used for example in some herbicides, was situated in Seveso village in Northern Italy. Due to negligent action of a plant worker, the chemical boiler overheated, which led up in discharge of about six tons of toxic gases, including one kilogram of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. Evacuation of the area was reported to take several days. First signs of the emissions were the dead animals found on the streets. As a result, over 80 000 animals were slaughtered in order to avoid further contamination of humans through the digestion. Few days after, people started feeling nausea, blurred vision and first signs from chloracne were observed. This accident has led to enactment of very strict legislation for chemical handling and storage in the industry. (EU Environmental Accidents (Seveso III), About.com)

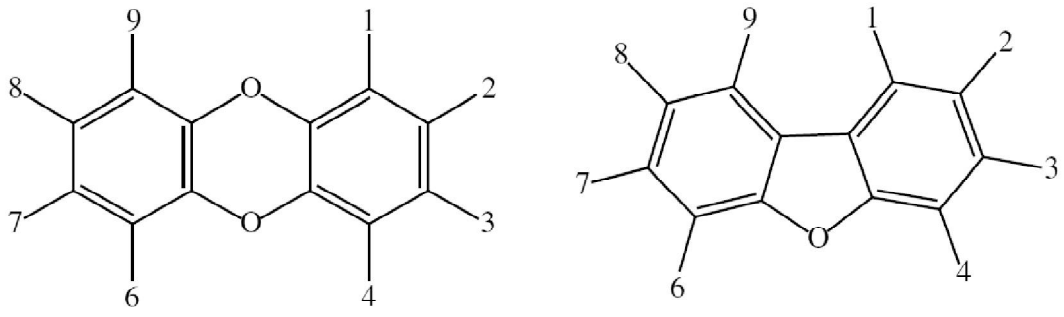
Today, dioxins and furans are mainly generated and released to the environment from several chemical and thermal processes. Among other, these include waste incineration, demolition wood and coal combustion, pulp bleaching, various processes in cement and metal industry, chemical manufacturing, and cremation. Dioxins and furans can also accumulate in the environment to be released further or to be transported to new areas. They may also be formed from structurally related precursors, such as phenols, through biological and chemical reactions. In addition, dioxins are released in volcanic eruptions and forest fires. (Kulkarni et al. 2008, p. 4-5)

Despite the large amount of dioxin sources, waste incineration is the main source of dioxins and furans today. In waste combustion processes, all the basic elements required for extensive dioxin formation are present in sufficiently high concentrations. These elements include oxygen, chlorine, carbon source (fly ash), catalyst (metals), and a proper 'temperature window'. The dioxin concentration in waste combustion flue gases may vary from about 1 up to 500 ng/m^{3}n given in international toxic equivalents (I-TEQ). However, due to advanced flue gas cleaning technologies the emission limit of 0.1 ng/m^{3}n I-TEQ used in many countries is achievable. (Kulkarni P. et al. 2008)

At most of the waste incineration and waste combustion plants, the dioxin emission that is emitted from the stack is remarkably under the emission limit. This means, that the best available technology for waste combustion allows lower emissions to the environment. Therefore, it may be expected that the international emission limit will be lowered some day in the future. If not, at least the emission limit for certain individual boilers may be tightened. Despite the high performance of flue gas cleaning devices, the formation of dioxins in the waste combustion process should be minimized. For this reason, the fundamentals of formation and mitigation of dioxins should be understood.

2.3 Chemical structure and biological effect of PCDD/Fs

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are groups of polychlorinated aromatic compounds. Dioxins and furans, as they are called for short, have similar physical and chemical properties and biological effect, whereupon they are generally discussed together. The chemical structure of PCDD and PCDF is shown in Figure 2.1. (Altarawneh M. et al. 2009. p. 2) Dioxins and furans consist of two benzene rings, one (PCDF) or two (PCDD) oxygen atoms, and varying amount of chlorine and hydrogen atoms connected to the aromatic ring structure. PCDD/Fs can have one to eight chlorine atoms, and the position and the number of chlorine atoms define the specific congener of each molecule. Each numbered location can be positioned either by a hydrogen atom or a chlorine atom. This will result in 75 possible congeners of dioxins and 135 congeners of furans; in total, 210 different congeners of PCDD/Fs exist. (Altarawneh M. et al. 2009, p. 2)



Dibenzo-*p*-dioxin **Dibenzofuran**

Figure 2.1. *Constitutional structure of PCDD and PCDF. (Altarawneh M. et al. 2009)*

Despite the large amount of different PCDD/F congeners, only 7 congeners of dioxins and 10 congeners of furans are extremely toxic and persistent ones. They are said to have a “dioxin-like” characteristic. All of these compounds have chlorines in 2-, 3-, 7-, and 8-positions and only those seventeen congeners are generally included in emission measurements. However, consideration of each individual congener is essential in order to study and understand the behavior of PCDD/Fs in the environment and thermal processes. (Fiedler H. 2003, p.5)

Dioxins are usually called as super toxins, because even an extremely low exposure may cause serious harm to humans or animals. The 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TeCDD) represents one of the most toxic compounds ever made by a human. (Fiedler H. 2003, p. 5) PCDD/F exposure may cause danger to humans, including increased risk of severe skin lesions, altered liver function, general weakness, depression of the immune system, changes in activity of liver enzymes, and abnormalities of endocrine and nervous system. 2,3,7,8-TeCDD is found to be carcinogenic, and it may cause congenital disabilities and harm the fetus. (Fiedler H. 2003, p. 24) In addition, dioxins belong to persistent organic pollutants (POP), and they accumulate in the food chain, more precisely, in the animal fat. Therefore, even an extremely small dioxin emission rate might be harmful to the environment, animals, and human beings. The exposure to humans takes place mostly through digestion, by eating meat, milk products, eggs, fish, and other similar products. (Fiedler H. 2003, p. 1)

2.4 International Toxic Equivalency Factors (I-TEF) of PCDD/Fs

Due to the large number of PCDD/F isomers, the measurement of each component would be onerous. In the 1980’s, when the common interest towards measuring of dioxins emerged, the PCDD/F emission was measured based on homologue groups (consisting of congeners of same amount of chlorine atoms); the total dioxin emission that was reported was sum of different PCDD/F homologues. Since the toxicities of different isomers vary, the measured total emission was not found to be a very good approximation of the biological and chemical effect of the total PCDD/F emissions. As a result, lists of different toxic equivalency factors (TEFs) were introduced by several organizations. (A. J. Chandler & Associates Ltd. 2006, p. 98)

The TEF values of the most toxic 17 congeners are given in relation with the toxicity of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TeCDD) and these congeners are responsible of the overall toxicity of PCDD/F mixture. 2,3,7,8-TeCDD is considered to be the most toxic PCDD/F congener, thus having a TEF reference value of 1. A list of different toxicity equivalent factors is shown in Table 2.1. The International Toxicity Factors (I-TEF), which are the most commonly used, were introduced in 1988 by the North Atlantic Treaty Organization (NATO) with support of the Committee on Challenges of Modern Society (CCMS). (Fiedler H. 2003, p. 29) The new IE-directive,

which was released in 2010, for instance, uses I-TEFs. More recently, the World Health Organization has introduced own recommendations, termed as WHO-TEFs. Other toxicity factors that may be in use are Nordic and Eadon. The difference between the factors must be considered when analyzing emission measurement reports.

Table 2.1. *Different toxic equivalent factors; Nordic, Eadon, International toxic equivalency factors (I-TEFs), WHO's recommendations (WHO-TEF$_{98}$). (A. J. Chandler & Associates Ltd. 2006, Raiko R. et al. 2002)*

Congener	**Nordic**	**Eadon-86**	**I-TEF**	**WHO-TEF$_{98}$**
2,3,7,8-TeCDD	1	1	1	1
1,2,3,7,8-PeCDD	0.5	1	0.5	1
1,2,3,4,7,8-HxCDD	0.1	0.033	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.033	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.033	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0	0.01	0.01
OCDD	0.001	0	0.001	0.0001
2,3,7,8-TeCDF	0.1	0.33	0.1	0.1
1,2,3,7,8-PeCDF	0.001	0.33	0.05	0.05
2,3,4,7,8-PeCDF	0.5	0.33	0.5	0.5
1,2,3,4,7,8-HxCDD	0.1	0.021	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.021	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.021	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.021	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0	0.01	0.01
OCDF	0.001	0	0.001	0.0001

The sum of the 2,3,7,8-substituded PCDD/F congeners weighted by the toxicity factors is called toxicity equivalent (TEQ). Respectively, different toxicity equivalents are marked as I-TEQ, WHO-TEQ$_{98}$, et cetera. Of these, the I-TEQ is the most commonly used toxicity equivalent. (A. J. Chandler & Associates Ltd. 2006, p. 99) Utilization of toxicity equivalents allows simple comparison of harmful PCDD/F emissions with only one value. The PCDD/F emission limit for waste incineration plants in the European Union is 0.1 ng/m^{3}n (I-TEQ). (D 2010/75/EU, p. 69)

3 BASIC FORMATION ROUTES OF PCDD/FS IN WASTE COMBUSTION PROCESSES

Since the late 1970's when the dioxins were found in the municipal waste incinerator flue gases and fly ashes (Olie K. et al. 1977), the formation of dioxins in waste incineration processes has been widely investigated. It has been concluded that the main formation routes include; high temperature gas phase formation (pyrosynthesis), catalytic formation from organic precursors on fly ash particles, and catalyzed formation from residual carbon backbone in presence of inorganic chlorine (de novo synthesis). (Tuppurainen K. et al. 1998, p. 3-4) In this chapter, the PCDD/F formation routes will be reviewed in detail.

3.1 Through pass of already-existing PCDD/Fs in waste

One possible reason for dioxin emissions in the flue gas is incomplete destruction of already-formed dioxins in the waste fuel. It has been reported (Abad E. et al. 2002) that significant amounts of dioxins may already be present in the waste fuel. 22 different Spanish municipal solid waste samples were analyzed; the dioxin concentration in these samples varied between 1.55 and 45.16 ng/m^3n I-TEQ/kg_{fuel}, suggesting that the significance of the existing dioxins in waste on the final emission is difficult to predict.

Abad E. and his co-workers (2002) carried out several measurements including calculations of the dioxin mass balance over a grate-fired municipal waste incinerator. They found out that the result of the mass balance depended mainly on the PCDD/F concentration in the fuel, because the output PCDD/F level remained rather constant during different measurements, but the input PCDD/F concentration varied greatly. Later inspection of the congener distributions (fingerprints) evidenced that the dioxins are almost completely destroyed at the high temperature zone of the furnace and further generated in the post-furnace zone at lower temperatures. (Abad E. et al. 2002, p. 6)

It has been numerically calculated that the destruction of PCDD/Fs occurs rapidly at higher temperatures (Shaub W. & Tsang W. 1983, p. 4). The PCDD/F concentrations that are allowed in stack, however, are less than one billionth of a gram in a standard cubic meter of flue gas. The reaction time in the furnace is probably not enough to allow complete destruction of the PCDD/F molecules. The level of destruction will depend highly on the performance of the combustion and mixing of the fuel and combustion air. However, other formation pathways than the through pass of already-existing dioxins through the entire combustion process seem to be mainly responsible of the PCDD/F emissions in the stack. (Abad et al. 2002)

3.2 Formation of PCDD/F precursors

The formation of PCDD/Fs is a result of incomplete combustion. In the ideal situation, the hydrocarbons in the fuel will convert to H_2O and CO_2 in presence of oxygen. However, the combustion air is not likely to reach every single particle of the fuel and a complete decomposition of the hydrocarbons does not occur. This leads to incomplete oxidation of carbon, which results in more complicated reactions and alternative products, such as acetylene and ethylene. Also, different radicals, such as $CH_3^{\bullet}$ or $CHCl^{\bullet}$ may be formed. This is followed by high temperature synthesis, where a grand variety of different hydrocarbons is generated. This includes aliphatic hydrocarbons C_xH_y (e.g. methane, ethane) and aromatic hydrocarbons (e.g. benzene, phenol, chlorinated phenol). (Raiko R. 2002, p. 371)

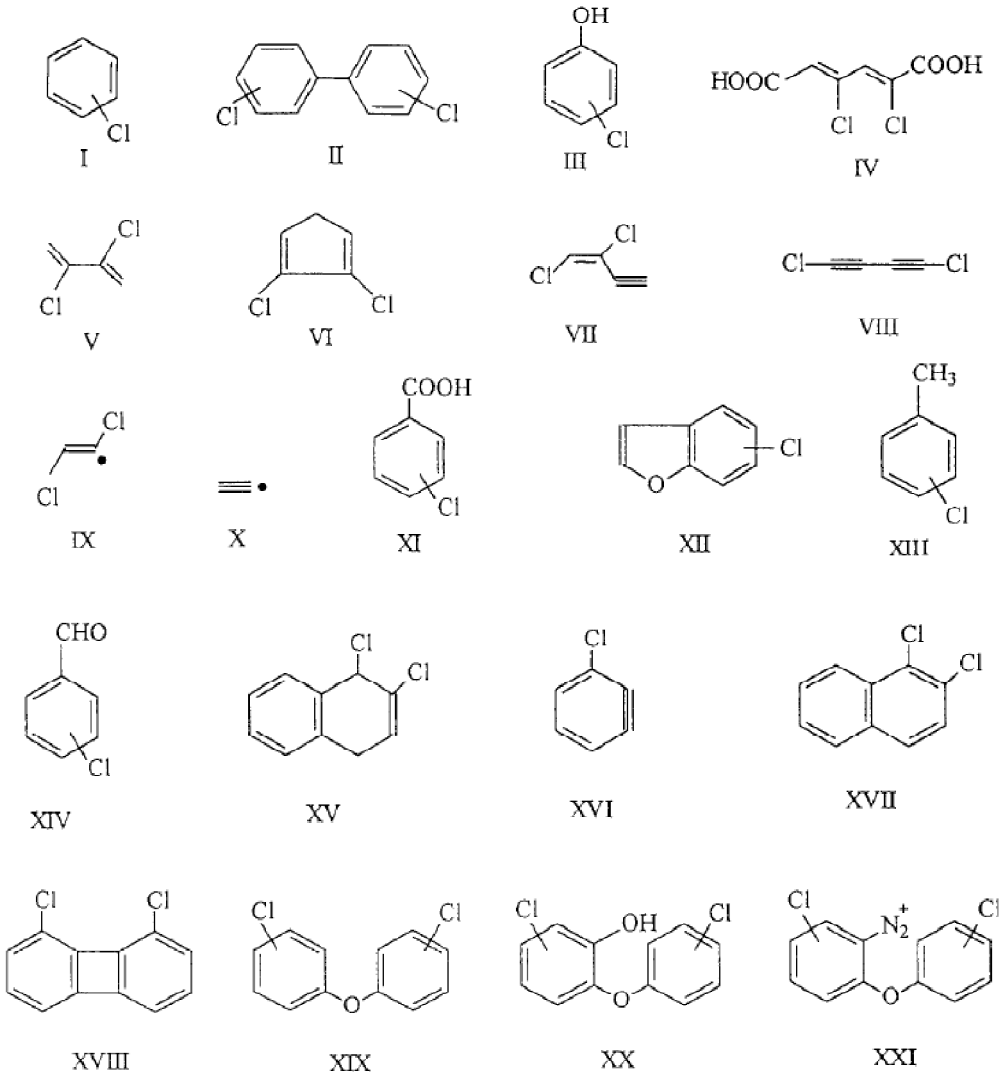


Figure 3.1. *Some potential precursors of PCDD/Fs. (Tuppurainen K. et al., p. 6)*

The formation of different hydrocarbons may be followed by further formation of polycyclic aromatic hydrocarbons (PAHs) or PCDD/Fs. The production of PICs (products of incomplete combustion) is supposed to take place mostly at 750 °C. Since

an enormous amount of different compounds may act as precursors for PCDD/F formation, an immeasurable amount of possible formation routes and reactions exists. Some possible precursors, which were reviewed by Tuppurainen K. et al. (1998), are shown in the Figure 3.1 above. The following chapters will discuss some of the main PCDD/F formation pathways. (Bajamundi C. 2011, p. 12-14; Raiko R. 2002, p. 371)

3.3 Homogeneous formation of PCDD/Fs

High temperature gas phase formation of PCDD/Fs at temperatures from about 500 to 800 ºC is commonly known as *pyrosynthesis* and it is considered to be a homogeneous formation pathway. Several compounds can act as precursors for gas phase formation of PCDD/Fs, however, monocyclic aromatic compounds, such as chlorinated phenols or chlorobenzenes, are considered to be the most important precursors. Gas phase formation is supposed to have a minor role in the overall dioxin formation process compared to heterogeneous reactions which will be introduced in Chapter 3.4. (Altarawneh M. et al. 2009, p. 2)

Due to the grand variety of possible precursors, an armoury of different gas phase formation routes exists. These reactions include, among others, formation of different radicals, oxidation and chlorination reactions, cyclization and aromatization reactions, and formation of C-C bonds. (Tuppurainen K. et al. 1998) Closer investigation and analysis of gas phase reaction mechanisms would require extremely profound examination on the thermodynamics and kinetics of PCDD/F formation from different compounds and consideration of a number of possible formation reactions. In purpose of giving an impression of the diversity of PCDD/F formation, one important formation pathway from phenol, which is found to be one of the key precursors for PCDD/Fs, is described in the Chapter 3.3.1 below.

3.3.1 Homogeneous formation of PCDD/Fs from phenol precursors

The gas phase formation of PCDD/Fs from phenols is believed to consist of three steps (Altarawneh M. et al. 2009, p. 4):

1. Self-condensation of the precursors
2. Cyclization of the initial intermediates from the first step to produce PCDDs and PCDF.
3. Chlorination/dechlorination reactions.

The first step includes cyclization reaction between *one chlorophenoxy radical and one chlorophenol molecule, two chlorophenoxy radicals*, or *two chlorophenol molecules.* Phenoxy radicals, $C_6H_5O^{\bullet}$, are formed in pyrolytic conditions from chlorophenols. They will decompose to mainly CO and cyclopentadienyl cyc-C_5H_5 in combustion processes. However, they may also form important intermediates for PCDD/F through so called self-dimerization processes, which are presented in Figure 3.2 below (Altarawneh M. et

al. 2009, p. 5). Dimerization refers to formation of a compound (dimer) from two similar monomers. (Zumdahl S. 2005, p. 1033, 1037)

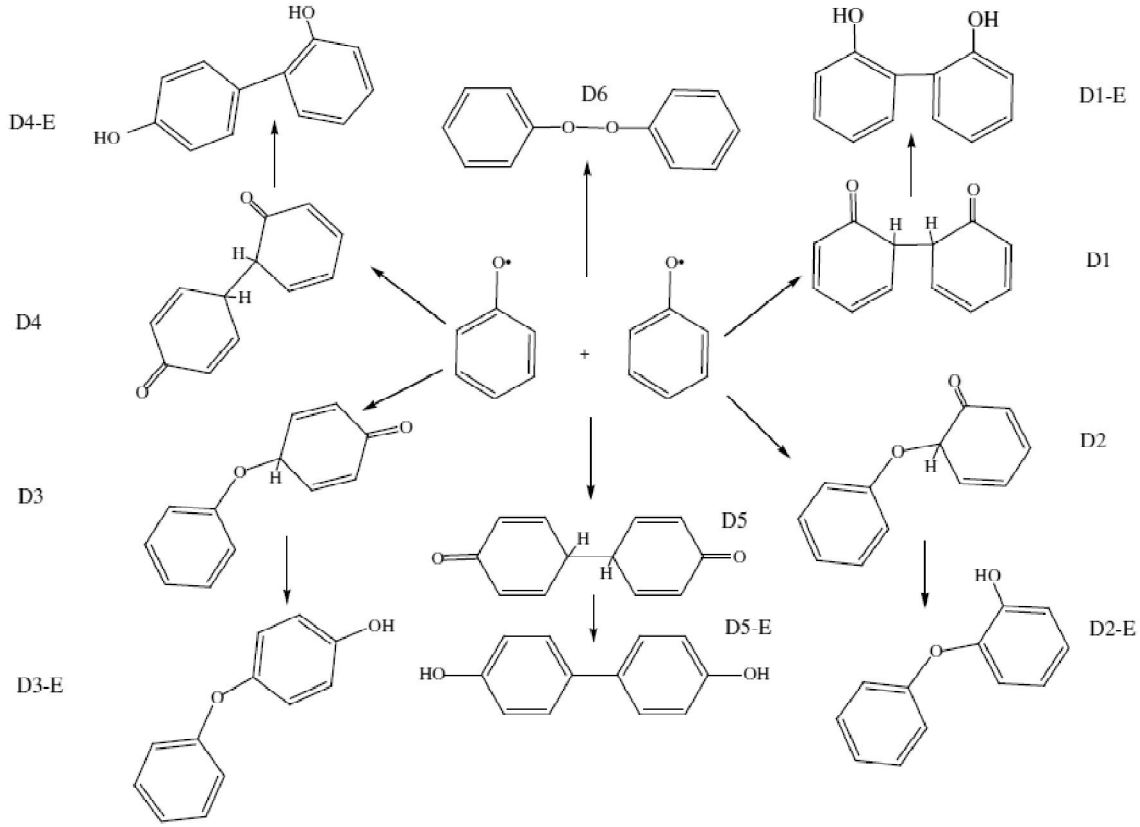


Figure 3.2. *Products of self-dimerization of phenoxy radicals (D1-D6) and their corresponding product structures (D1E-D5E). (Altarawneh et al. 2009 p. 5)*

The second step involves various cyclization reactions to form unchlorinated dibenzo-*p*-dioxins and dibenzofurans (DD/DFs) or PCDD/Fs. One example of this is the formation of dibenzofurans (DF) from D1-E-intermediate, which is shown in Figure 3.3. This intermediate is found to possibly be one key intermediate for PCDF formation in the gas phase. (Weber R. & Hagenmaier H. 1999a)

Alternatively, the second step may involve, for instance, coupling of 2,4,6-trichlorophenoxy radical and 2,4,6-trichlorophenol through which PCDD molecule is formed, as presented by Wiater I. et al. (2000) The schematic picture of the reaction is shown in Figure 3.4 below.

The third step of gas phase formation from phenol is supposed to consist of a number of chlorination and dechlorination reactions (Altarawneh M. et al. 2009 p. 4, 6-7), which will be discussed in detail in Chapter 3.5.

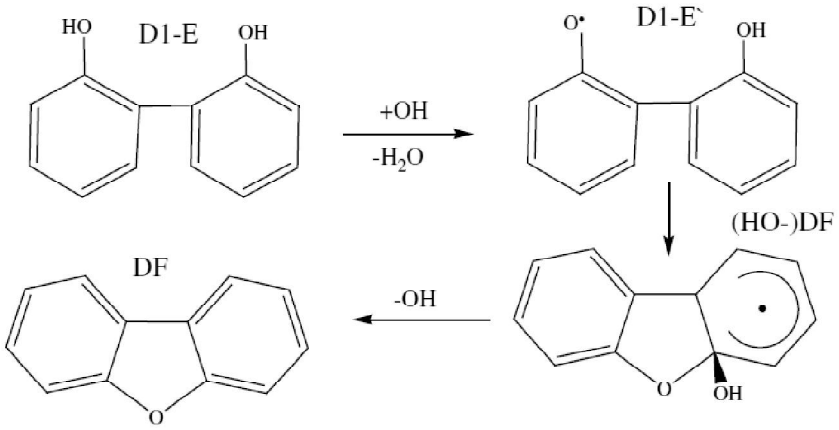


Figure 3.3. *Formation of dibenzofurans from D1-E intermediate. (Born J. et al. 1989, see Altarawneh et al. 2009, p. 6)*

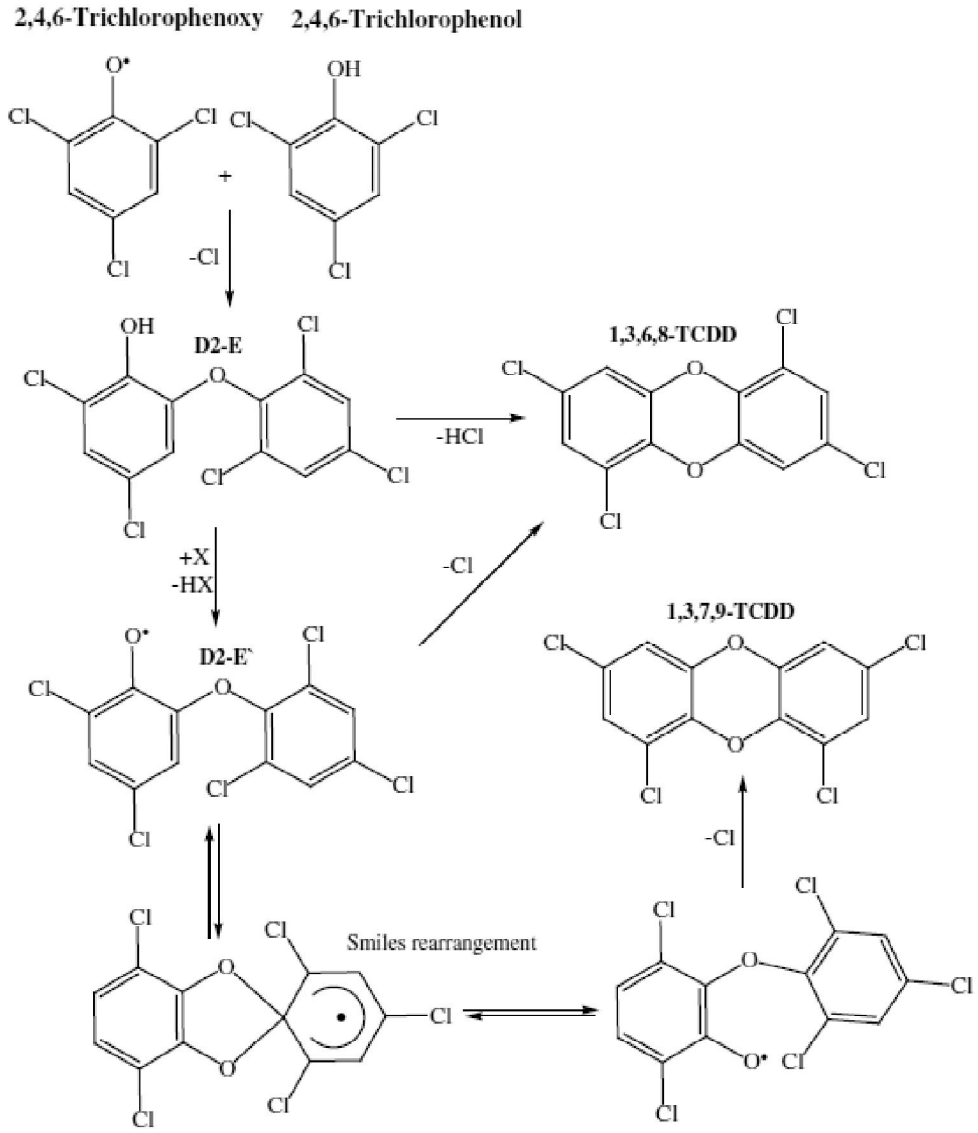


Figure 3.4. *Formation of PCDD from the coupling of 2,4,6-trichlorophenoxy radical and 2,4,6-trichlorophenol. (Wiater I. et al. 2000, see Altarawneh et al. 2009, p. 7)*

3.3.2 Other homogeneous formation routes of PCDD/Fs

In addition to the above-described mechanisms, other homogeneous routes have been suggested. One possible pathway in the gas phase includes oxidation of polychlorinated benzenes (PCBz) at temperatures above 300 ºC. (Sommeling P. M. et al 1994, see Altarawneh M. et al 2009) PCDD/Fs may also be formed from more complex compounds containing similar structures with PCDD/Fs. For example, permethrin and tebuconazole (Figure 3.5) are synthetic compounds widely used as a pesticide and fungicide, respectively, and as a raw material for wood preservatives. These compounds are found to produce large amounts of PCDD/Fs when exposed to oxidative conditions. (Tame N. et al. 2007) PCDD/Fs may also be formed from pyrolysis of hydroquinone compounds, which can be formed from thermal degradation of biomass or burning of tobacco. (Altarawneh M. et al. 2009, p. 11)

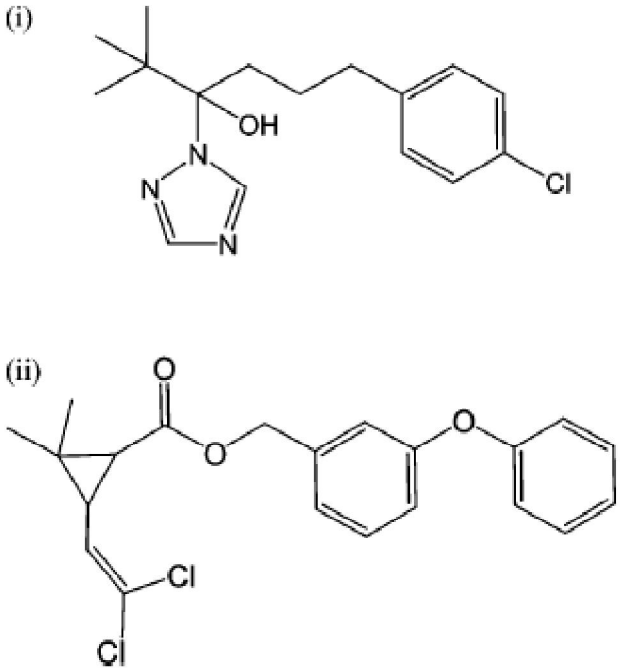


Figure 3.5. *Chemical structure of tebuconazole (i) and permethrin (ii). (Tame N. et al. 2007, p. 2)*

3.4 Heterogeneous formation of PCDD/Fs

Heterogeneous formation pathways refer to PCDD/F formation in the post-combustion zone at temperatures of about 200 to 500 ºC in presence of a catalyst. Heterogeneous formation routes are found to play a significant role in the PCDD/F formation in waste incineration plants. The most important heterogeneous formation routes may be divided in two mechanisms; *precursor mechanism* and *de novo synthesis.* In this Chapter, these two formation pathways are reviewed in detail.

3.4.1 Precursor mechanism

The formation of PCDD/Fs via condensation of structurally related precursors on the surface of a catalyst (copper in fly ash) is usually known as *precursor pathway* or *precursor mechanism*. The most important precursors include phenol (Ph), benzene (Bz), and their chlorinated fellows; chlorophenols (CPh) and chlorobenzenes (CBz). Both phenols and benzenes are found to form dioxins and furans through condensation reactions. Of these, chlorophenols are found to be much more active than chlorobenzenes. Therefore, phenols and chlorinated phenols are usually considered to be the most important precursors for PCDD/F production through precursor mechanism. (Addink R. et al. 1995c)

The optimal temperature range for precursor mechanism is from about 200 to 500 ºC. (Ryu J.-Y. et al. 2005b) The formation through catalyzed precursor pathways is generally supposed to take place faster than the formation from carbon matrices (de novo synthesis, see the following chapter). (Addink R. et al. 1995b, p. 9) However, opposite findings of the formation rates have also been concluded. (Everaert K. & Baeyens J. 2002, p. 3) The formation through precursor pathway is generally said to favor more the formation of dioxins than furans. (Altarawneh M. et al. 2009, Dickson L. et al 1992, Everaert K. & Baeyens J. 2002) It is also found to be responsible of production of higher chlorinated PCDDs, whereas gas phase formation from precursors (Chapter 3.3) would prefer the formation of lower chlorinated PCDDs (Mulholland J. & Ryu J.-Y. 2001). Due to the large amount of possible precursors, PCDD/F congeners, and reaction conditions, various routes of catalytic precursor pathways exist and a simple and straightforward definition of precursor mechanism does not exist.

The formation of PCDD/Fs through precursor mechanism was comprehensively investigated by Lomnicki & Dellinger (2002). They proposed two major pathways for PCDD/Fs on a copper-catalyst surface; *Langmuir-Hinshelwood* reaction and *Eley-Rideal* reaction. Both reactions are bimolecular reactions on metal surfaces. The Langmuir-Hinshelwood reaction (Figure 3.6) involves adsorption of two chlorophenoxy radicals on a Cu-surface, which then form a 4,6-DCDF through various intermediates. This mechanism could be responsible of the formation of furans. The first step of the Eley-Rideal reaction (Figure 3.7) is the adsorption of a 3-chlorocatecol, the concentration of which was directly correlated to PCDD yield in the laboratory-scale test. Then, it is supposed react with a gaseous chlorophenol. This is followed by desorption of dibenzo-*p*-dioxin molecule from the copper surface. This route could be responsible of the formation of dioxins.

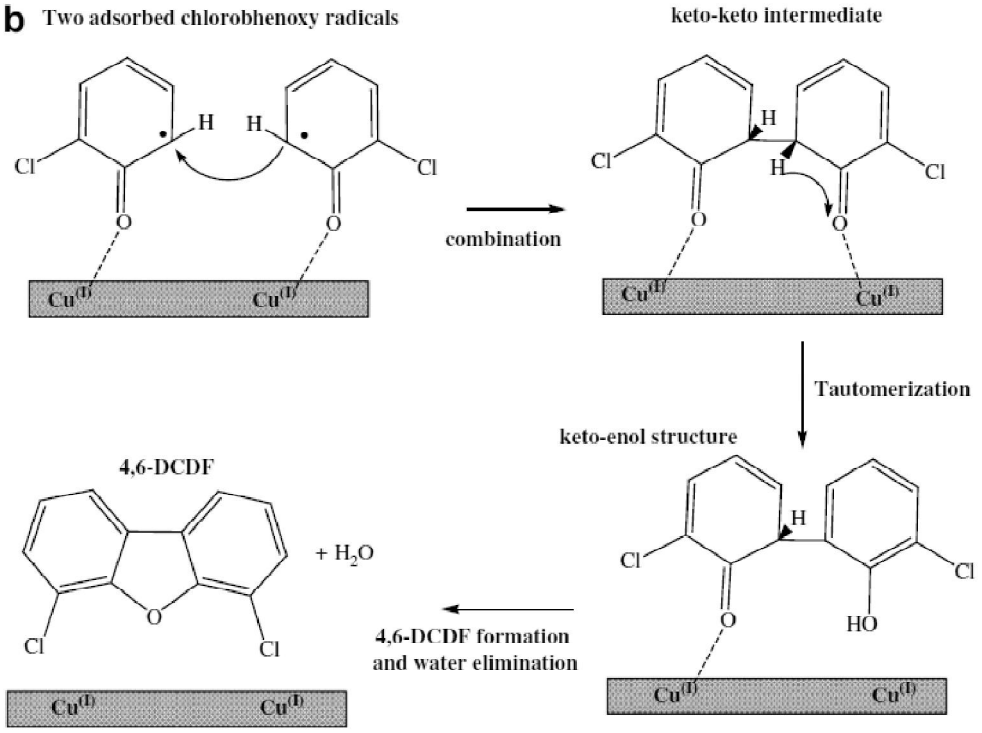


Figure 3.6. *The proposed Langmuir-Hinshelwood mechanism. (Lomnicki S. et al. p. 5; Altarawneh M. et al. 2009, p. 13)*

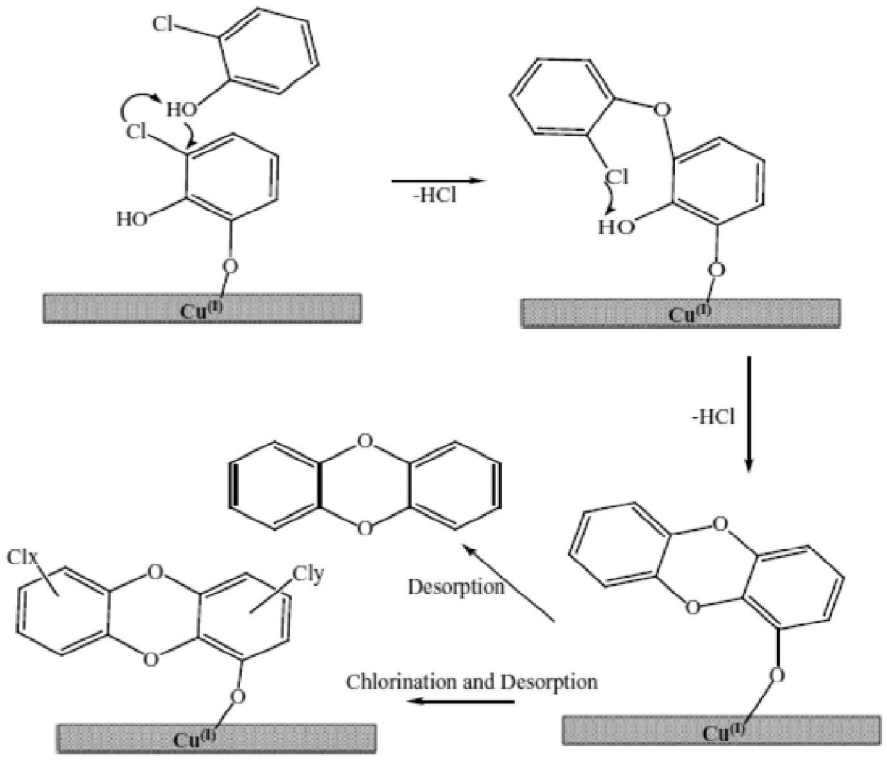


Figure 3.7. *The proposed Eley-Rideal mechanism. Formation of PCDD on a CuO-surface. (Lomnicki S. et al. 2002, p. 5; Altarawneh et al. 2009, p. 13)*

3.4.2 De novo synthesis

De novo synthesis refers to PCDD/F formation pathways which include breakdown of carbon matrices (residual carbon) through several oxidation and chlorination reactions on the surface of a catalyst (copper in fly ash). (Altarawneh M. et al. 2009, p. 15). The temperature window for de novo synthesis is from about 200 to 450 ºC, reaching the maximum rates at about 300 ºC. (Suzuki K. et al. 2004, p. 2; Everaert K. & Baeyens J. 2002, p. 3) De novo synthesis is commonly accepted to generate more furans than dioxins. (Addink R. et al. 1995b) Since the concentration of furans is usually much higher in flue gases from municipal waste incinerators (MWI) than the concentration of dioxins, de novo synthesis is supposed to be the major PCDD/F formation route in waste incineration processes. (Everaert K. & Baeyens J. 2002, p. 9) A schematic picture of formation of PCDFs through de novo synthesis is shown in Figure 3.8.

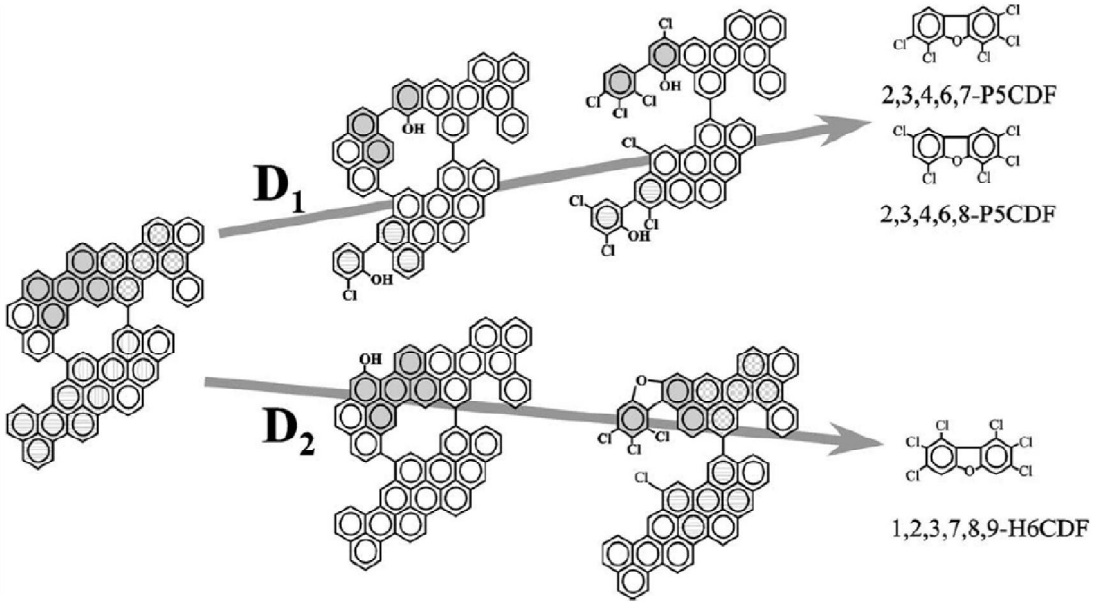


Figure 3.8. *An illustrative picture of the formation of PCDF from a carbon matrix via de novo synthesis through two different oxygen insertion mechanisms (D1 and D2). (Weber R. et al. 2001, p. 8)*

De novo synthesis requires the following factors to occur: fly ash deposit, oxygen, chlorine, desirable temperature window, and a catalyst. The presence of copper in various forms is found to remarkably enhance PCDD/F formation through de novo synthesis. (Fujimori T. et al. 2007, p. 1) The role of copper will be comprehensively discussed in the following chapters. Iron compounds are also found to catalyze PCDD/F formation through de novo synthesis, however it seems to be less active than copper. (Addink R. et al. 1995b) A straight correlation between the fly ash content in the flue gases and the concentration of PCDD/Fs has been found (M. Altarawneh et al. 2009, p. 15). The amount of fly ash and the fly ash characteristics clearly play a key role in PCDD/F formation.

Addink R. et al. (1995b) studied PCDD/F formation in the fly ashes in presence of a copper catalyst. They concluded that PCDD/F formation took place for a long period of time, up to several hours. This finding suggests that PCDD/F formation through de novo synthesis mainly occurs in fly ash deposits, where flue gas passes over the fly ash bed. Therefore, the back pass of the boiler and flue gas cleaning devices, such as electrostatic precipitators (ESP) or fabric filters (FF) operated above 200 ºC, are possible places for PCDD/F formation via de novo synthesis. De novo formation in the fly ash, that travels quickly through the optimal temperature region (residence time up to few seconds), was found to be almost nonexistent.

3.5 Chlorination and dechlorination reactions

Once dibenzo-*p*-dioxin (DD) and dibenzofuran (DF) molecules are formed, they can be followed by several chlorination and dechlorination reactions, which seem to have a significant role in PCDD/F formation and in the development of congener distributions (fingerprints). In this chapter, the main chlorination reactions will be presented.

3.5.1 The role of chlorination reactions in a MSWI

Most of the flue gases chlorine is present as hydrogen chloride (HCl), which is usually considered to be an inactive form of chlorine in formation of dioxins. HCl, however, may be transformed to more active chlorinating agents, such as chlorine atom $Cl^{\bullet}$ or molecular chlorine Cl_2, both of which are considered to be more active chlorinating agents than HCl, particularly in the PCDD/F formation from precursors. (Wikström E. et al. 2003a, p. 6) Metal chlorides are also found to play a significant role in chlorination reactions. (Altarawneh M. et al. 2009, Hatanaka T. et al 2003)

Chlorination reactions are usually connected with the formation of furans. Addink R. et al. (1996a) investigated chlorination of dibenzofurans (DF) as a potential formation pathway of PCDF in a model fly ash in presence of HCl. They concluded that chlorination of dibenzofuran yields mainly 2,3,7,8-substituded congeners. The chlorination process follows electrophilic substitution reaction (see Chapter 3.5.2). They suggested that all possible PCDF congeners could be formed through this pathway.

Ryu J.-Y. et al. (2004) examined the potential role of chlorination reactions in the formation of PCDD/Fs in municipal waste incinerators. They ended up with similar conclusions; the chlorination pathways seem to have a significant role in the formation of furans, but the formation of dioxins would be governed by other pathways, such as condensation of phenol precursors.

3.5.2 Chlorination of aromatic hydrocarbons in pyrolytic conditions

Chlorination may also take place before the formation of DD/PCDD and DF/PCDF molecules. For instance, chlorination of aromatic hydrocarbons, such as benzenes or phenols, may occur in the gas phase, in pyrolytic conditions. This is found to be a

remarkable chlorination pathway. In case of benzene, C_6H_6, the first step is direct abstraction of hydrogen atom by Cl, thus resulting in formation of a phenyl molecule C_6H_5, and an HCl molecule. Under pyrolytic and chlorine rich conditions, the formation of C_6H_5 molecule is followed by absorption of a Cl atom from the surroundings, which results in formation of a chlorobenzene molecule C_6H_5Cl. Repeating of this reaction will result in higher chlorinated aromatics. (Altarawneh M. et al. 2009)

3.5.3 Chlorination of carbon matrices by gaseous chlorine

The residual carbon backbones of different structure found in the fly ash are usually called as carbon matrices. One important chlorination pathway presented by Altarawneh et al. (2009) involves the *transfer of gaseous chlorine into the carbon matrix*. As suggested, the overall reaction may take place through the following routes:

1. Replacement of hydrogen in the carbon matrix by Cl atom
2. Addition of $Cl^{\bullet}$ into the carbon matrix or
3. Chlorination of the existing aromatic compounds in the carbon matrix by electrophilic substitution.

Electrophilic substitution reactions (route 3) are typical for aromatic hydrocarbons, such as benzene, and for saturated hydrocarbons. In the reaction, an electrophile (Cl in this case) substitutes a functional group (H atom). Usually, a catalyst, such as $FeCl_3$ (Figure 3.9) or $AlCl_3$, is required in these kinds of substitution reactions of aromatic compounds. The order of chlorination in electrophilic substitution reactions is the following; 2, 8, 3, 7, 1, 4, 6, 9, which was further proved to coincide with experimental results. (Addink R. et al. 1996a) Aliphatic hydrocarbons would rather undergo an addition reaction. (Zumdahl S. 2005, p. 1024-1025)

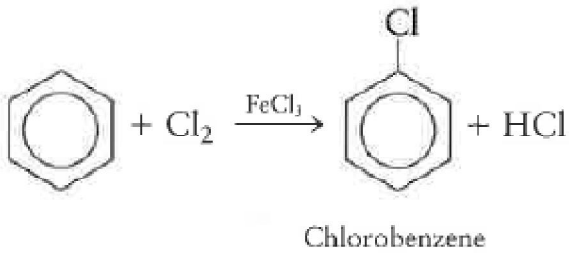


Figure 3.9. *Substitution of hydrogen atom by Cl in presence of $FeCl_3$-catalyst. (Zumdahl S. 2005, p.1024)*

3.5.4 Chlorination of carbon matrices by inorganic chlorine

Another important chlorination reaction involves *transfer of inorganic chlorine* into the carbon matrix. This reaction is called *ligand transfer*. While various copper and iron compounds can participate in this mechanism, $CuCl_2$ is used as an example. The mechanism includes:

$$R \cdots H + CuCl_2 = RHCl^* + CuCl \quad (1)$$
$$RHCl + CuCl_2 = RCl + CuCl + HCl, \quad (2)$$

where *R* denotes the aromatic compound, such as benzene or phenol. The basic reaction can be seen in Figure 3.10 below.

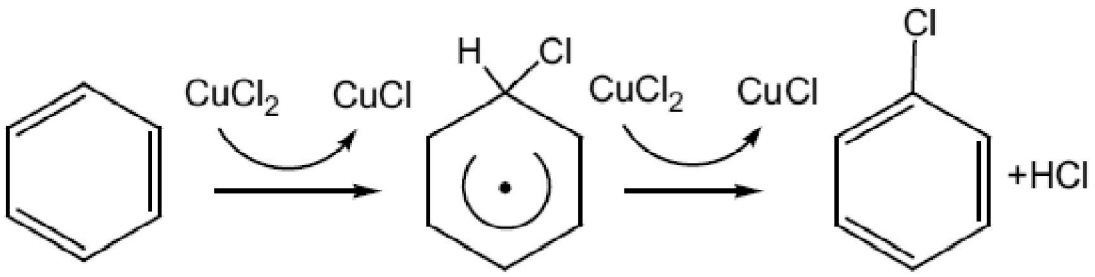


Figure 3.10. *Schematic diagram of chlorination by $CuCl_2$ via ligand transfer. (Altarawneh M. et al. 2009, p. 22)*

The overall reaction can be written as

$$RH + 2CuCl_2 = RCl + 2CuCl + HCl. \quad (3)$$

These reactions are followed by the oxidation cycle, which includes the following reactions:

$$CuCl + \tfrac{1}{2}O_2 = CuCl \cdots O^* \quad (4)$$
$$CuCl \cdots O^* = CuO + \tfrac{1}{2}Cl_2 \quad (5)$$
$$CuO + 2HCl = H_2O + CuCl_2 \quad (6)$$
$$CuCl \cdots O^* + 2HCl = H_2O + CuCl_2 \quad (7)$$

After these reactions, $CuCl_2$ enters again the catalytic cycle. The Ligand transfer is found to act as an important chlorinating pathway of carbon matrices in the fly ash. (Altarawneh M. et al. 2009)

3.5.5 Dechlorination of PCDD/Fs

Dechlorination refers to reactions, in which higher chlorinated PCDD/Fs lose chlorine atoms to form less chlorinated congeners. These reactions are comprehensively studied by Iino F. et al. (2000). They build up a prediction model for formation of PCDD/F from octachlorinated dioxins and furans via dechlorination reactions. The data from several MWIs were compared with the prediction models. The dechlorination of OCDFs was found to play an important role in formation of PCDF isomer patterns. The

predicted models of PCDD distribution did not coincide with the sampled data, suggesting that chlorination plays only a minor role in formation of PCDDs.

The dechlorination reactions in the fly ash are also found to play a minor role when a chlorinating agent is present (Addink R. et al. 1996a), thus the degree of chlorination of different PCDD/F congeners seems to be a balance between chlorination and dechlorination reactions.

4 THE EFFECT OF COMBUSTION CONDITIONS AND POST-COMBUSTION CIRCUMSTANCES

Combustion of waste creates a favorable environment for PCDD/F formation. In this chapter, the influence of the key parameters on PCDD/F formation in the furnace and in the post-furnace zone will be presented. Combustion performance highly depends on the fuel load and fuel characteristics, bed and combustion temperature, and mixing of the fuel with the combustion air. Post-furnace circumstances, such as temperature, chlorine and oxygen concentrations, moisture, residence time in the favorable 'temperature window', and fly ash composition are found to remarkably influence the PCDD/F formation. (Aurell J. et al. 2009, p.1) Understanding their effect on PCDD/F formation could offer a tool for hindering the formation of PCDD/Fs.

4.1 The effect of temperatures and residence times

The temperature is one key element of PCDD/F formation in waste incineration processes. When PCDD/F emissions from waste incineration are discussed, waste incinerator plants are usually divided in two zones; the furnace, where the combustion process takes place, and the post-combustion zone, where the flue gas is cooled and cleaned by proper flue gas cleaning equipment (and where PCDD/Fs are mainly formed). The correct temperature together with sufficient residence time will create the 'window of opportunity' for PCDD/F formation.

4.1.1 The furnace temperature and quality of combustion

It is generally accepted that the formation of PCDD/Fs could be significantly limited by offering sufficient residence time of the combustion gases at high temperature zone of the furnace. In waste incineration, a residence time of two seconds at above 850 ºC is required (D 2010/75/EU, p. 41), and it is also used as a basis for boiler designing. This recommendation is given to allow sufficient combustion performance and to minimize the formation of PICs and aromatic precursors. It is also considered as the best available technology (BAT) at the moment. (Jätteenpoltto BREF 2006, p. 60)

Aurell J. et al. (2009) carried out experiments in a laboratory-scale fluidized bed incinerator (5 kW) in purpose of studying the effect of different combustion parameters on PCDD/F formation. The reduction of freeboard temperature to 660 ºC resulted in increased CO level, resulting most likely from incomplete combustion of the fuel. The

PCDD/F yield was three times higher compared to the reference run at 800 ºC, however, the dioxin/furan ratio, and homologue and congener patterns remained relatively constant. This indicated that the formation pathways were not influenced by the lower temperature. When the freeboard temperature was increased to 950 ºC, an increase in PCDDs was found, whereas the PCDF yield remained unchanged. At higher temperature the homologue profile of furans was shifted more towards higher chlorinated congeners, indicating of increased chlorination activity. However, no remarkable changes in PCDD/F congener patterns were found, which suggests that the change in temperature of the combustion zone does not have an effect on any specific formation pathway. (Aurell J. et al. 2009, p.6)

The furnace temperatures usually are higher than 850 ºC when operated at full load, which allows sufficient combustion of the fuel. However, when the fuel load is decreased intentionally or unintentionally, the temperature may remarkably decrease. The amount of unburned material exiting the furnace increases, thus resulting in higher production of PCDD/Fs in the post-furnace zone. In addition, the furnace temperature profiles vary. Especially, the temperature near the furnace walls can be hundreds of degrees below the required 850 ºC. This generates a possibility for certain fuel particles to travel through the combustion process in lower temperature regions, which increases the possibility of incomplete combustion. Good boiler design, good mixing of the fuel with the combustion air, and stable boiler operation are perquisite for low PCDD/F emissions.

4.1.2 Temperature and residence times in the post-combustion zone

The residence time of two seconds above 850 ºC in the furnace, however, does not assure dioxin-free emissions. Most of the PCDD/Fs are supposed to be formed in the post-furnace zone at about 650 to 200 ºC, where the flue gas is cooled down. (Tuppurainen K. et al. 1998, p. 2) In this temperature region, catalytic pathways (de novo synthesis and precursor mechanism) are supposed dominate (see Chapter 3). Therefore, the residence time in this temperature region should be limited and the flue gas should be quickly cooled down below 200 ºC, where the PCDD/F production rates are significantly decreased. The time required for PCDD/F formation is less than a second. This would mean that the flue gas velocity over the eco area should be around 20 m/s (generally approx. 6 m/s) using existing heat exchangers, which is relatively difficult to implement. However, faster cooling of the flue gases results in lower amount of PCDD/Fs. (Fängmark I. et al. 1994)

On the other hand, it has been suggested that high cooling rates of the flue gas of high temperatures and sufficient oxygen concentrations would allow favorable circumstances for chlorination of PCDD/Fs. $Cl^{\bullet}$ radicals may be formed from Cl_2 molecules even at relatively low temperatures (500 ºC) from reactions between HCl and O and OH radicals. (Wikström E. et al. 2003a, p. 3) If the flue gas is cooled quickly, the $Cl^{\bullet}$ radicals may not have enough time to recombine to Cl_2 or HCl. The abundance of

$Cl^{\bullet}$ radicals may then lead to high chlorination rates of hydrocarbons, including phenols, benzenes, and PCDD/Fs. (Altarawneh M. et al. 2009, p. 17)

The operating temperature of flue gas cleaning devices is usually discussed as an important parameter for PCDD/F formation at lower temperatures (300 to 200 ºC) at which the fly ash deposits together with sufficient residence times increase the possibility of PCDD/F production and the possibility of release of particle phase dioxins to the gas phase. At this temperature region, fly ash deposits together with flue gas flow passing over the fly ash surfaces may generate a continuous dioxins source. The more fly ash is deposited and the higher the temperature is, the higher the possibility for PCDD/F production or release from particle to the gas phase will be. (Lundin L. 2013)

A clear correlation between the ESP temperature and PCDD/F emissions at several MSWIs has been reported. Therefore, it is recommended that the ESP should be operated at below 200 ºC. (Everaert K. & Baeyens J. 2002, p. 8-9) Opposite conclusions have also been made; Wikström E. and her co-workers (2000) suggested that most of the PCDD/Fs and other aromatic compounds, such as DD/DFs, biphenyls, benzenes and phenols, would be formed at higher temperatures >650 ºC, which would be followed by chlorination reactions at the lower temperature zone, and the role of de novo synthesis at these temperatures would be only minor.

Mätzing H. et al. (2001) observed that the temperature and chemical properties of the fly ash particles were found to be the major factors affecting the gas-solid partitioning. This would be an important factor in the relation of ESP operating temperature and PCDD/F emissions released from the ESP; at higher temperatures more dioxins escape to the gas phase, which allows them to exit the ESP more easily.

4.2 Different forms of chlorine as chlorinating agents

One major reason for high PCDD/F emissions from combustion of solid waste is the high chlorine content in waste fuels. The content of chlorine in typical municipal solid waste (MSW) is reported to be approximately 4.6%-w of dry MSW (2.8%-w of wet MSW). (Kanters M. et al. 1996) The chlorine content is lower, about 1%, in treated waste, such as solid recovered fuel (SRF) used in CFB boiler plants.

In waste combustion processes, chlorine may be present as ash-bound chlorine, which may act as a direct chlorine source in PCDD/F formation. (Wikström E. et al. 2003a, p. 2) In addition, chlorine may be present as gaseous compounds, such as HCl, Cl_2, or $Cl^{\bullet}$, which are also found to act as significant chlorine sources in PCDD/F production. (Addink R. et al. 1995b) Gaseous chlorine species, such as HCl and Cl_2 are supposed to offer a chlorine source mostly for PCDD/F formation from precursors, whereas PCDD/F formation through de novo synthesis is found to receive sufficient amounts of chlorine from the ash-bound chlorine. (Wikström E. et al. 2003a, p. 2)

4.2.1 Metal chlorides as a chlorine source

Chlorine can be present as solid form in the fly ash as inorganic chlorine, such as metal chlorides ($CuCl_2$, CuCl) or alkali and alkaline earth metal chlorides (KCl, NaCl, $MgCl_2$). KCl is also found in large amounts in gaseous form in the flue gases. They may also be present as organic chlorine in extractable form (chlorinated aromatics) or inextractable form directly attached to the carbon matrix with C-Cl bonds. (Wikström E. et al. 2003a)

The activity of metal chlorides as a chlorinating agent is found to be much higher compared to earth metal chlorides. (Addink R. & Altwicker E. 2001) In addition, the activity of chlorine that is already present in the fly ash (carbon matrices) is found to be significant. This suggests that both the metal chlorides and the chlorine that is already attached to the carbon matrices with C-Cl bonds may act as important chlorine sources for PCDD/Fs, and the role of alkali and alkaline earth metal chlorides is only minor. Especially, the role of copper chlorides in fly ash catalyzed formation and chlorination reactions of PCDD/Fs is commonly accepted. (Takaoka M. et al. 2008; Ryu J.-Y. et al. 2003; Fujimori T. et al. 2007)

4.2.2 Gaseous forms of chlorine and Deacon-process

In conventional municipal solid waste incinerators, most of the flue gas chlorine is present as HCl (Wikström E. et al. 2003a, p. 3), which is usually considered to be an inert form of chlorine in formation of dioxins and furans. Molecular chlorine, Cl_2, instead, is supposed to be a more active chlorinating agent. HCl can be converted to molecular chlorine through so called Deacon-process, which is a $CuCl_2$-catalyzed reaction. Higher concentration of chlorine may result in higher formation rate of PCDD/Fs. Deacon-process is usually considered to be an important participant in PCDD/F formation. (Altarawneh M. et al. 2009, p. 20)

The basic reaction can be presented by the equation

$$2HCl + \frac{1}{2}O_2 \leftrightarrow Cl_2 + H_2O, \quad (8)$$

in which the two-way arrow signifies that the reaction can occur in both ways. Therefore, the amount of HCl and Cl_2 in the flue gas is always a state of equilibrium depending on many factors, such as temperature. (Gullett B. 1990)

The formation of Cl_2 from HCl through Deacon-process was investigated by Gullett B. et al. (1990) by means of temperature, HCl concentration, and different catalysts. The highest conversation rate of HCl to Cl_2 was reached at about 440-450 ºC, which falls to the temperature window of PCDD/F formation. The reaction was found to occur rapidly, indicating that the reaction does not depend on time. The conversion was found to be independent of HCl concentration (250 to 1500 ppm). By contrast, the oxygen concentration was found to increase Cl_2 yield intensively until 3%, after which the HCl

to Cl_2 conversion-% remained at a constant level (at about 45%). This suggests that the oxygen concentrations in the flue gas channels of conventional waste incinerators would not limit the formation of Cl_2 through Deacon-process, because the oxygen concentration is generally more than 3%. The reaction was found to occur equally when different forms of copper were used as catalysts; Cu, Cu_2O, and CuO. The addition of water vapor seemed to transfer the equilibrium of reaction to the left side of the reaction (8), as may be expected.

4.2.3 HCl as a chlorinating agent

Addink R. et al. (1995a) questioned the role of Deacon-process as major pathway for chlorination of PCDD/Fs. They tested both HCl and Cl_2 as chlorinating agent and compared the yields of PCDD/F. The total yield was almost equal in both cases but the homologue distribution was different. They concluded that Deacon-process was not the major pathway for chlorinating of PCDD/Fs.

Also, the PCDD/PCDF ratio varied between Cl_2 and HCl as a chlorinating agent, although the total PCDD/F yield remained relatively constant. Cl_2 as a chlorinating agent favored the formation of furans. Moreover, they found out (Addink R. et al. 1996) that chlorination by HCl occurred also in absence of oxygen, which is required in Deacon-process. These findings suggest that other chlorination pathways than Deacon-process must exist. These pathways may include also the formation of PCDD/Fs directly from HCl.

Kanters M. et al. (1996) investigated the formation of chlorophenols from combustion of municipal solid waste. They concluded that significant amounts of chlorophenols may be formed from HCl, which can then act as chlorinated precursors for PCDD/Fs.

4.3 The presence of oxygen and moisture

Oxygen is an important element in PCDD/F formation, because all dioxin and furan molecules involve oxygen atoms. Moreover, oxygen is required for de novo synthesis and other dioxin-related reactions, such as the Deacon-process. Nevertheless, it is important to ensure that enough oxygen is present in the combustion process to allow sufficient combustion of the fuel, because the PCDD/F concentration is found to significantly increase due to poor oxygen supply simulating transient combustion conditions (Aurell J. 2009, p. 4)

On the other hand, lower O_2-concentrations in the flue gas are found to decrease PCDD/F emissions, assuming that the combustion process is accomplished properly. Therefore, the amount of oxygen in the combustion process should be optimized in order to minimize PCDD/F emissions. The PCDD/F homologue patterns are found to remain unchanged in varying oxygen concentrations indicating that the formation pathways would be independent of the level of the oxygen. (Zhang H.-J. et al. 2008, p. 2, 6)

The presence of water in the flue gas has been reported to slightly decrease PCDD/F formation at the post-combustion temperatures (240-650 ºC). (Wikström E. et al. 2003b) This might be explained by the change in the equilibrium of Deacon-process towards the side of HCl. In addition, the presence of water seems to enhance carbon degradation to CO and CO_2, which will result in lower PCDD/F concentrations. A shift towards lower chlorinated congeners was also observed due to addition of H_2O, which indicates that the H_2O in the gas phase enhances dechlorination of PCDD/Fs. Aurell J. et al. (2009) reported that no significant variations in PCDD/F formation were observed due to addition of water, except of minor increase in the PCDD/PCDF ratio, suggesting that water has no major effects on any specific formation pathways.

4.4 The effect of the amount of fly ash and fly ash particle size

It has been reported that the amount of fly ash directly correlates to the amount of PCDD/Fs emitted. (Altarawneh M. et al. 2009, p. 15) This is due to the high concentration of residual carbon (Kakuta Y. et al. 2005), metal (copper) chlorides (Takaoka M. et al. 2005b), and other active species (Weber R. et al. 2002) found in municipal solid waste fly ashes. The fly ash composition highly depends on the process, fuel properties and additives fed into the process. The fly ash particle size distribution will likely have an effect on PCDD/F formation due to increased active surface area in the fly ash of smaller particle sizes. The fly ash particle size, particle density, physical (e.g. porosity) and chemical properties of the fly ash particles, and the PCDD/F vapor pressure are shown to have influence on the PCDD/F formation and the PCDD/F partitioning between the gas phase and solid phases. (Mätzing H. et al. 2001)

The amount of fly ash varies in different types of boilers. In grate-fired boilers, the amount of fly ash of the total amount of ashes is significantly lower (about 35%) compared to fluidized bed boilers (from about 50% up to 90%) and the amount of bottom ash is higher in grate-fired boilers than in FB boilers, respectively. (DeFusco J. et al. 2007) Higher amount of fly ash will likely increase the risk of PCDD/F formation in the post-furnace zone of fluidized bed boilers.

In fluidized bed boilers, the fly ash is collected in various stages; in the convection section, in bottom of the economizers and air preheaters, and finally, in the dust collection devices. As mentioned before, dioxins are supposed to be formed in this temperature region (200 to 650 ºC) and the flue gas passing over the dust deposits in different parts of the flue gas channels will probably act as unwanted dioxin sources. Therefore, the fly ash emitted from the furnace would rather correlate to the dioxins emitted than the fly ash levels of the flue gas entering the dust collecting devices.

5 THE MAIN CATALYSTS AND INHIBITORS IN PCDD/F FORMATION

Fly ashes from municipal waste incineration contain plenty of different metals (Olie K. et al. 1997). Several metal chlorides (e.g. $MgCl_2$, $ZnCl_2$, $FeCl_2$, $MnCl_2$, $HgCl_2$, $CdCl_2$, $NiCl_2$, $SnCl_2$, $PbCl_2$, and $CuCl_2$) (Stieglitz L. et al. 1989, see Olie K. et al. 1997) and metal oxides (e.g. TiO_2, CuO, Cu_2O, Fe_2O_3, see Figure 5.1) (Qian Y. et al. 2005, Gullet B. 1990) are found to promote formation of PCDD/Fs. Of these compounds, however, only copper chlorides and copper oxides are found significantly contribute to PCDD/F formation. On the other hand, it is also shown that alkaline earth metal oxides, such as MgO and CaO (Qian Y. et al. 2005) have suppressing effect on PCDD/F formation. Furthermore, various sulfur (Addink R. et al. 1996b; Samaras P. et al. 2000) and nitrogen (Tuppurainen K. et al. 1999; Samaras P. et al. 2000; Ruokojärvi P. et al. 2001a, 2001b) compounds are usually considered to inhibit PCDD/F formation. In this chapter, the main catalyzing and inhibitive compounds are reviewed.

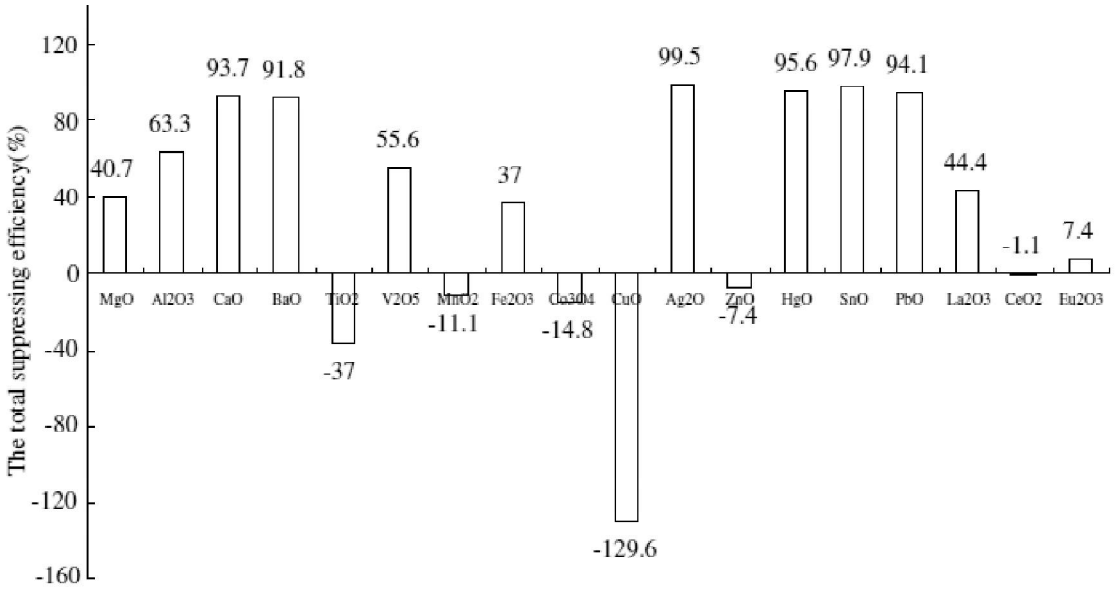


Figure 5.1. *The suppressing efficiencies of various metal oxides at 280 ºC during a two-hour test. (Qian et al. 2005. p. 4)*

5.1 Copper as a catalysts in PCDD/F formation

Municipal solid waste contains notable amounts of different metals. (Kanters M. et al. 1996; Olie K. et al. 1997) The presence of copper is found to remarkably enhance the

formation of PCDD/F, and it is commonly recognized to be the most important catalyst and one of the key elements required for PCDD/F formation in municipal waste incinerators (MWIs). (Raiko R. et al. 2002; Hatanaka T. et al. 2003; Qian Y. et al. 2005) Both the copper oxides (Lomnicki S. & Dellinger B. 2002) and copper chlorides (Takaoka M. et al. 2008; Mulholland J. et al. 2001) are found to catalyze PCDD/F formation. Even a minor Cu-content of about 0.07%-w (Hatanaka T. et al. 2003, p. 3) in the MSW fly ashes is shown to highly enhance the PCDD/F production.

The role of copper is diverse. As it was mentioned before (Chapter 4.2.2), copper seems to play a key role in Deacon-process as a catalyst. It is also involved in important chlorination reactions through ligand transfer (Chapter 3.2.3), though in this case copper act as a direct chlorinating agent. It clearly plays a vital role in PCDD/F production via de novo synthesis and precursor mechanism. (Fujimori T. et al. 2007; Hatanaka T. et al. 2003) Copper may also have reductive behavior in PCDD/F formation by catalyzing several decomposition and oxidation reactions of PAHs to less toxic products, such as carbon monoxide. However, copper compounds clearly promotes rather the formation than the destruction of PCDD/Fs. (Altarawneh M. et al. 2009, p. 22)

5.1.1 Change in elemental forms of copper in the fly ash

Copper may appear in the fly ash in different forms, among others including the following species:

- Atacamite ($CuCl_2 \cdot 3Cu(OH)_2$ or $Cu_2(OH)3Cl$), which is the most abundant species in the real fly ash at room temperature.
- Copper oxides, such as CuO and Cu_2O,
- Copper chlorides CuCl, $CuCl_2$ and $CuCl_2 \cdot 2H_2O$, and
- Elemental copper Cu.

Generally, copper chlorides, especially $CuCl_2$, are considered as the most important catalysts. (Fujimori T. et al. 2007, Takaoka M. et al. 2005b) Copper(II)oxide, CuO, is found to be most active catalyst of copper oxides in production of PCDDs. (Gullett B. et al. 1992a, see Altarawneh M. et al. 2009, p. 12) CuO is also capable of acting as an oxidizing agent for PCDD/Fs in oxygen-free conditions. (Lomnicki S. & Dellinger B. 2002, p. 3)

One interesting matter is the change in chemical forms of copper at different temperatures. The fractions of elemental copper Cu(0), cuprous compounds Cu(I), and cupric compounds Cu(II) in different MSWI and model fly ashes were studied (Takaoka M. et al. 2005b). At room temperature, copper was found in the following forms and factions; $CuCl_2 \cdot 3Cu(OH)_2$ (75%), Copper(I)chloride CuCl (14%), and copper(II)hydroxide $Cu(OH)_2$ (11%). As the temperature was further raised to 300 ºC, the distribution was transformed into CuCl (45%), Cu (29%), and Cu_2O (26%), respectively. At this point, drastic changes in the forms could be observed;

$CuCl_2 \cdot 3Cu(OH)_2$ was no longer present in the fly ash, and CuCl was the most abundant species. Finally, when the fly ash was heated to 400 ºC, the fraction of CuCl increased to 60%, whereas Cu and Cu_2O were both responsible for 20% of the total Cu-content, respectively. This clearly demonstrates the temperature dependence of different forms of copper. This change in forms of copper by temperature variation may partly explain the temperature window of de novo synthesis. (Takaoka M. 2005b)

5.1.2 The importance of copper chlorides in the fly ash

Copper(II)chloride or cupric chloride ($CuCl_2$) is involved in a large number of reactions related to PCDD/F formation, such as Deacon-process. In the literature, $CuCl_2$ is usually considered to be the most catalyzing form or copper and a significant chlorine source in the fly ash. The formation of PCDD/F through $CuCl_2$-catalyzed chlorination of phenol precursors has also been profoundly investigated by Ryu J-Y. et al. (2002; 2005a).

Ryu J.-Y. et al. (2003) studied chlorination of PCDD/Fs by $CuCl_2$ and they observed that the consumption of $CuCl_2$ was high, almost 100%, as measured both in terms of DD/DF converted to PCDD/Fs and $CuCl_2$ consumed. They concluded that two moles of $CuCl_2$ was converted to CuCl per each transferred Cl atom. This coincides with the reaction method of ligand transfer (Chapter 3.5.4). The maximum yield was reached in temperatures between 200 and 300 ºC (Ryu J.-Y. et al 2003), which seems to be an optimal temperature region for several PCDD/F-related reactions.

Takaoka M. et al. (2005b) investigated the effect of different forms of copper on the formation of chlorinated aromatics in the MSWI fly ashes. First, the chemical forms of copper in eight different MSWI fly ash samples were determined. Then, the relationship between the formation of chlorinated aromatics (CBz, PCBs) and different copper compounds was specified. The most abundant copper species were copper chlorides $CuCl_2 \cdot 3Cu(OH)_2$ and CuCl. In only one of the MSWI fly ash samples copper chloride compounds were not found, and the copper was present as CuO (36%) and $Cu(OH)_2$ (64%) leading to relatively low yield of PCBs and CBz. This argues that copper chlorides are essential for the formation of chlorinated aromatics, but they may not always appear in real fly ashes. (Takaoka M. et al. 2005b)

5.2 Reduction of PCDD/F formation by sulfur

In municipal waste incinerators dioxin emissions are traditionally controlled by flue gas cleaning devices, such as electrostatic precipitators (ESP), fabric filters (FF)/bag house filters (BHF), scrubbers, and additive feeding. These facilities are expensive and any need for additional devices results in high investment costs. A better alternative would be trying to diminish the formation of PCDD/Fs already in the flue gas channels. Sulfur is one of the main compounds that are found to have inhibiting effects on PCDD/F formation. The inhibitive effect of sulfur addition is reported to efficient when sulfur is fed into the process during long period of time.

At some plants, sulfur is fed into the combustion process for other purposes, such as corrosion mitigation, thus the technology is already available and it may offer a simple method for PCDD/F reduction. The possible inhibition routes and the overall effect of sulfur addition will be discussed in this chapter.

5.2.1 Possible routes of inhibition of PCDD/F formation by SO_2

Several sulfur compounds from pure sulfur to SO_2 and more complex compounds, such as sulfonic acids and sulfamides, are found significantly reduce PCDD/F concentrations in MSWI flue gases. (Samaras P. et al 2000, Ryan S. et al. 2006) Another example of the effect of sulfur is co-firing of coal in municipal waste incinerators, which is found to reduce dioxin emissions. This might occur partly due to more efficient combustion achieved by the addition of coal, but higher concentrations of SO_2 in the flue gas may also be responsible of the PCDD/F reduction. (Ryan S. et al 2006; Yan J.-H. 2006) However, additional sulfur in the process may lead to increased need for flue gas cleaning (reduction of SO_2).

In laboratory-scale experiments, over 95% reduction efficiencies by addition of sulfur compounds have been reported. (Samaras P. et al. 2000) While the reductive effect of increased SO_2 level in the flue gas seems to be apparent, the reactions through which the reduction takes place remain somewhat unclear.

One possible route is homogeneous pathway by direct reduction of Cl_2 to HCl (Gullett B. et al. 1992b), which can be expressed by equation

$$Cl_2 + SO_2 + H_2O \rightarrow 2HCl + SO_3. \quad (9)$$

Another possible route is the formation of sulfates from metal chlorides or metal oxides (e.g. $CuCl_2$, CuO). As one example, this pathway may include the reaction

$$CuO + SO_2 + \tfrac{1}{2}O_2 \rightarrow CuSO_4. \quad (10)$$

This process (reaction 10) is also known as the Shell-process that is used to reduce sulfur oxides and nitrogen oxides from the flue gases. (Raiko R. et al. 2002, p. 351) Metal sulfates, such as $CuSO_4$, are found to be less active catalysts for Deacon-process and for biaryl synthesis (PCDD formation from phenols) (Gullett et al. (1992b). The lower catalytic activity is supposed to result from lower number of active sites of $CuSO_4$ molecules for chlorination and oxidation reactions. Ryan S. et al. (2006) also agreed with the theory of formation of metal sulfates in the fly ash as the main suppressing mechanism.

Finally, SO_2 may reduce PCDD/F formation by participating in other PCDD/F formation routes, such as condensation of ring precursors, thus resulting in sulfur analogues polychlorinated dibenzothiophenes (PCDTs) or polychlorinated thianthrenes (PCTAs). (Gullett et al. 1992b)

In purpose of defining the main PCDD/F reduction pathway in which SO_2 is involved, the effect of SO_2-addition in different combustion conditions was studied in a lab-scale reactor simulating combustion and post-combustion zones of a conventional MSWI. The addition of SO_2 in the post-combustion flue gases clearly reduced both PCDD and PCDF concentrations, reaching concentrations of about one third of the initial emission. An important fact is that the reduction was significantly higher for PCDFs than for PCDDs. The isomer and homologue profiles remained relatively unchanged which indicates that there is a reduction in total PCDD/Fs, not only transfer of already formed PCDD/Fs to different congeners. (Ryan S. et al. 2006)

The experiment also involved injection of Cl_2 and SO_2 into the reactor at 400 ºC in purpose of studying the interaction between SO_2, Cl_2, HCl and PCDD/Fs. In the base case (Cl_2 injection, no SO_2, no fly ash present), the yield of HCl from Cl_2 was about 20%. When SO_2 was added, a slight increase (10%) in Cl_2 to HCl conversion was observed. This suggests that the role of homogeneous conversion of Cl_2 to HCl through the reaction 9 would be only minor in post-combustion zone circumstances. However, when the test was repeated in presence of fly ash (C 1.0%, chloride 5.7%, Cu 0.17%, Fe 0.95%, S 6.4 ppm) without SO_2-injection, the yield of HCl was doubled compared to the base case. Finally, the test was carried out with SO_2 injection in presence of fly ash. Almost complete conversation of Cl_2 to HCl was observed and the consumption of SO_2 was high. This suggests that the conversion of Cl_2 to HCl by SO_2 is a fly ash-catalyzed reaction, which may play a key role in PCDD/F prevention by SO_2. (Ryan S. et al. 2006)

5.2.2 Formation of metal sulfates

One important conversion route is the formation of metal sulfates and HCl from metal chlorides in the fly ash. Ryan S. et al. (2006) noticed that insufficient amount of metal chlorides were present in the fly ash to be responsible of all HCl produced, so, additional sources of chlorine must exist. They proposed that metal oxides in the fly ash could have been transferred to metal chlorides in presence of Cl_2. This could be followed by transfer of metal chlorides to metal sulfates in presence of SO_2. Following reactions were introduced:

$$Cu_2O_3(s) + Cl_2(g) \rightarrow 2CuOCl(s) + \tfrac{1}{2}O_2 \qquad (11)$$

$$2CuOCl(s) + \tfrac{1}{2}O_2 + 2SO_2(g) + H_2O(g) \rightarrow 2CuSO_4(s) + 2HCl(g). \qquad (12)$$

The test took place at 300 ºC, which is an optimal temperature for PCDD/F formation. The formation of metal sulfates from metal chlorides would significantly reduce formation of PCDD/Fs via de novo synthesis, because metal sulfates are not shown to possess major catalytic activity. This may explain the higher inhibition rate of furans (Ryan S. et al. 2006; Aurell J. & Marklund S. 2009), because de novo synthesis is

reported to produce more furans than dioxins. In contrast, the effect on precursor pathways being responsible of PCDD formation would be minor. The metal chloride/metal sulfide ratio in the fly ash, which was found to correlate with the flue gas Cl/S ratio, was suggested to be directly related to the PCDD/F emissions. (Ryan S. et al 2006, p. 7) Significant reduction in PCDD/F production was earlier reached with flue gas S/Cl ratio of 0.64. (Raghunathan K. & Gullett B. 1996)

5.2.3 The effect of sulfur addition in the combustion zone and during unstable boiler operation

Ryan S. et al. (2006) also investigated the effect of sulfur in the combustion zone. The degree of chlorination was clearly decreased, thus shifting the balance towards lower chlorinated PCDD/Fs (mono- to trichlorinated congeners). Therefore, the amount of tetra- to octachlorinated congeners was smaller, thus a remarkable reduction in TEQ value was achieved. (Ryan S. et al. 2006, p. 5) However, if the amount of sulfur is too low, the dechlorination may only convert OCDDs and OCDFs towards tetrachlorinated DD/DFs, which could possibly result in higher TEQ value.

The effect of SO_2 addition during poor combustion conditions (sooting) was also investigated. (Ryan S. et al. 2006) The PCDD/F concentrations reported during the poor combustion experiment were much higher than in non-sooting conditions. The addition of SO_2 remarkably reduced PCDD/F emissions, especially PCDF emissions. Aurell J. & Marklund S. (2009) also concluded that the addition of SO_2 in the flue gases directly resulted in lower PCDD/F concentration during unstable operation. These findings indicate that higher SO_2 concentration of the flue gas during unstable combustion conditions would offer a tool for reducing PCDD/F emissions. (Ryan S. et al. 2006)

5.3 The role of additive feeding in the furnace

Different additives can be fed into combustion processes in purpose of reducing unwanted pollutants in the flue gases. These include several alkali metal, alkaline earth metal, and nitrogen compounds, such as $Ca(OH)_2$, $CaCO_3$, NaOH, and NH_3. They react with the pollutants in the combustion chamber, thus forming a neutral product which may easily be removed from the process. The effect of different additives on PCDD/F formation will be discussed in this chapter.

5.3.1 The effect of calcium-based additives on PCDD/Fs

Calcium compounds, such as limestone ($CaCO_3$), calcium hydroxide ($Ca(OH)_2$) or dolomite ($CaCO{\cdot}MgCO_3$) are often introduced to combustion processes in purpose of reducing acid gases (HCl and SO_2) from the flue gases. (Raiko R. et al. 2002, p. 353-355, 365-367) In addition to reduction of SO_2 and HCl, calcium compounds are shown to have an effect on PCDD/F formation. However, the effect may be negative or

positive, which should be considered when calcium-based compounds are used as sorbents. (Gullett B. et al. 1994; Lu S.Y. et al. 2007)

Lu S. et al. (2007) investigated the effect of different calcium compounds on PCDD/F emissions in high temperature combustion processes in a bench-scale system (~850 ºC). Pentachlorophenols (PCP) were used as precursors for PCDD/Fs. The addition of CaO was found to remarkably increase the formation of PCDD/Fs, when the Ca/Cl ratio was > 1. In contrast, the addition of $CaCO_3$ was found to significantly decrease the PCDD/F formation. Different behavior of CaO and $CaCO_3$ was explained by the different microstructure of the molecules (CaO is more porous) and by the participation of CaO in the formation reactions of PCDDs. Fly ash that contains CaO was also found to promote PCDD/F formation equally as pure CaO. The potential of CaCO3 as an inhibitor is also supported by Sun R.-D. et al. (2003).

Liu W. et al (2005) studied the inhibition of PCDD/F precursors by CaO in a laboratory-scale tests simulating post-combustion zone (280 to 450 ºC). The tests lasted for two hours to allow complete reactions. Inhibition efficiencies of up to 99% were reached when pentachlorophenols (PCP) were used as dioxin precursors. The highest inhibition rates were reached at about 300 ºC. They suggested that PCDD/F formation from precursors, such as chlorophenols, could be remarkably reduced by injection of CaO in the post-furnace zone at about 650 ºC. There it could absorb and decompose the dioxin precursors and the cooling process would take place in presence of CaO. It could also reduce HCl, which may act as chlorine source for PCDD/Fs. This experiment demonstrates the potential of CaO-feeding as a simple method for dioxin control.

The strong inhibitive effect of calcium hydroxide ($Ca(OH)_2$) is supported by many researchers. (Cheng Y.-C. 2005; Gullet B. et al. 1994) The reduction is supposed to take place both through the reduction in HCl and Cl_2 concentrations and through mechanisms that include the ash-bound chlorine (Gullet B. et al. 1994, p. 11). Weber R. et al. (2002) suggested that the presence of $Ca(OH)_2$ in fly ash would enhance PCDD/F degradation and dechlorination due to alkaline pH. In addition, PCDD/F reduction may likely due to adsorption of PCDD/F molecules on the $Ca(OH)_2$ molecules followed by removal of the sorbent particles from the process by ESP or fabric filter. (Gullett B. et al. 1994, p. 2) The dioxins problem, however, is only transferred elsewhere by the utilization of sorbents.

5.3.2 The effect of urea and ammonia on PCDD/Fs

A number of compounds containing nitrogen are also found to act as possible inhibitors for PCDD/F formation. The effect of addition of ammonia, NH_3, is believed to be only minor (Ishikawa R. et al. 1997), whereas the addition of urea, $CO(NH_2)_2$, is shown to result in lower PCDD/F emissions (Ruokojärvi P. et al. 2001a, 2001b) and it may serve as a simple method for PCDD/F reduction.

The potential of inhibition of different nitrogen (and sulfur) compounds in combustion of refuse derived fuel (RDF) was investigated by Samaras P. et al. (2000). The PCDD/F reduction efficiency of urea was found to be minor (28%) compared to

some sulfur compounds (up to 98%). Higher inhibition efficiencies (~50%) were later reported. (Samaras P. et al. 2001). The dioxins/furan ratios were found to remain relatively constant and the inhibition efficiency of urea addition was reported to be independent of the form in which it was fed to the process (solid or liquid). (Samaras P. et al. 2001)

Higher inhibition efficiencies by urea have been reported by Ruokojärvi P. et al. (2001a, 2001b), when urea was added to RDF feedstock of a pilot incinerator at 0.1, 0.5, and 1.0% of the fuel feed. The reduction in PCDD/F emissions varied from 35 to 47% in the gas phase and from 65 to 93% in the solid phase, resulting in total PCDD/F reduction of 64, 75, and 90%, respectively. Other tests have similarly concluded that the reduction mainly affects on the solid phase PCDD/Fs. (Tuppurainen K. et al. 1999, Ruokojärvi P. et al. 2001b) The PCDD/PCDF ratio increased when urea was added, thus indicating of different formation routes of dioxins and furans. The concentrations of chlorophenols were also affected, but only to a minor extent. The decomposition of urea is supposed to occur rapidly at high temperatures, and the real suppressing compounds may be other than urea itself. Therefore, utilization of other nitrogen compounds with same decomposition products may lead to similar results. (Ruokojärvi P. et al. 2001a)

Similar tests were also carried out by injecting urea (0.1, 0.5, and 1.0%-w) to flue gases, when combusting light heating oil. (Ruokojärvi P. et al 2001b) Again, the reduction was remarkably greater in the solid phase than in the gas phase. This may be due to “poisoning” of the active sites of the fly ash particles. Same conclusion was made by Tuppurainen K. et al. (1999). Maximum total reduction efficiency was reached at 0.5%-w of urea. Another important observation was that no reduction in chlorophenol concentrations was found, which differs from the earlier tests with urea (Ruokojärvi P. et al. 2001a) and from the tests with CaO as inhibitor, when almost all PCPs were absorbed and further decomposed in the reaction tube. (Liu W. et al. 2005, p. 3)

6 FLUE GAS CLEANING AND ITS ROLE IN PCDD/F FORMATION/REDUCTION

Nowadays in Europe, PCDD/F emission limits from power plants are strict (D 2010/75/EU) and they tend to be tightened. To meet with the required emission levels, industrial power boilers are always followed by certain combination of different flue gas cleaning devices. The extent of the system depends on the requirements to meet with the guaranteed emission limits. It is also important to consider future tendencies when acquiring new cleaning devices. Due to generating high emissions from waste combustion and due to the strict emissions limits, modern waste combustion plants are equipped with the latest flue gas cleaning technologies.

Since dioxins are mostly formed in the post-furnace zone, different flue gas cleaning devices are usually considered as possible places for dioxin formation when operated at the temperature region of PCDD/F formation. The role of different flue gas cleaning methods in PCDD/F formation, reduction and cleaning is discussed in this chapter.

6.1 Electrostatic precipitators

Electrostatic precipitators (ESP) are widely used for dust collection in industrial power plants. They are usually placed right after the air-preheaters, before other flue gas cleaning devices and they are often responsible for preliminary removing (about 60 to 90%) of fly ash particles from the flue gas. In modern power plants, ESPs are followed by other cleaning equipment, such as additive feeding and bag house filters, to offer optimal cleaning efficiency of the flue gas. (Oksanen A. 2004)

The cleaning method of an ESP is the following: the raw flue gas that is composed in the furnace and passes through the heat exchangers travels through a high voltage electric field (50-150 kV) that gives a negative charge to the dust particles. Then, the flue goes through a chamber that is filled with positively charged collector plates (grounded) and the particles with negative charge attach to the collector plates. The dust cake formed on the plates is regularly fallen off and the clean flue gas continues to the stack directly or through other cleaning devices. (Oksanen A. 2004)

It has been shown that the temperature of the ESP clearly correlates with the PCDD/F emissions. It is suggested that de novo synthesis would take place in the ESP even at temperatures below 200 ºC and the formation rates through de novo synthesis will increase with the operating temperature of the ESP. (Sierhuis W. & Born J. 1996) The reduced efficiency of particle capture may also due to standard temperature dependence of adsorption. (Everaert K. & Baeyens J. 2002)

ESPs are shown to capture well particle phase PCDD/Fs, whereas the gas phase PCDD/Fs may even increase in the ESP. The fraction of gaseous PCDD/Fs will likely increase, because more solid phase PCDD/Fs are precipitated in the ESP. It may also occur due to transfer of solid phase dioxins to gas phase. This applies especially for lower chlorinated congeners, which tend to appear in the gas phase due to higher vapor pressures compared to higher chlorinated congeners. (Guerriero E. et al. 2009)

The effect of electrostatic field has been suggested to increase PCDD/F formation in the ESP (Sierhuis W. & Born J. 1996). This was observed by calculating the mass balance of PCDD/F over an ESP of a MSWI when the ESP was switched on and off. The PCDD/F yield was relatively higher when the electric field was switched on. The electric field was found to have effect especially on the PCDD/F concentrations of the fly ash removed from the ESP indicating that the dioxins are formed in the fly ash deposits. However, the exact method through which the electric field affects on the formation remains unclear and further investigations on the effect of the electric field on PCDD/F emissions should be carried out.

6.2 Scrubbers

Scrubbers are flue gas cleaning devices that are used to remove gaseous (mainly SO_2 and HCl) components from the flue gas by alkaline solutions. Sorbents are usually calcium or sodium based compounds due to their ability to neutralize acid components of the flue gas by chemical or physical reactions. Plenty of different system designs and cleaning processes exists, but roughly scrubbers can be divided in two groups by the state of the reactants and end-products of the process; wet and semi-dry systems. (Raiko R. et al. 2002, p. 350-351; Oksanen A. 2004, p. 3.25-3.29) The investment and operating costs of different technologies highly differ by the amount of additives used and by the end products to be further processed. (Jätteenpoltto BREF 2006, p. 36)

In wet method, the flue gas is cleaned by solutions which will react with the flue gas components. This method is used to remove acid compounds, such as HCl and SO_2. Water solutions of $Ca(OH)_2$ or NaOH are commonly used as sorbents in wet scrubbers (Figure 6.1). The disadvantage of this method is the troubled handling of the wet and acid end-product. Semi-dry method involves spraying of liquid $Ca(OH)_2$ (limewater) in the flue gas stream. This will capture effectively acid (HCl) and sulfur compounds. The end product is dry and it exits the scrubber and is removed from the process in the fabric filters. Activated carbon may be sprayed also in purpose of removing heavy metals and dioxins. (Jätteenpoltto BREF 2006, p. 36-39)

In addition, a completely dry method which is not usually classified as a scrubber, involves spraying of dry sodium bicarbonate ($NaHCO_3$), $Ca(OH)_2$ or $CaCO_3$ and removal of dioxins and heavy metals by injection of activated carbon. The dry end product is removed as in the semi-dry method. (Jätteenpoltto BREF 2006, p. 36-39)

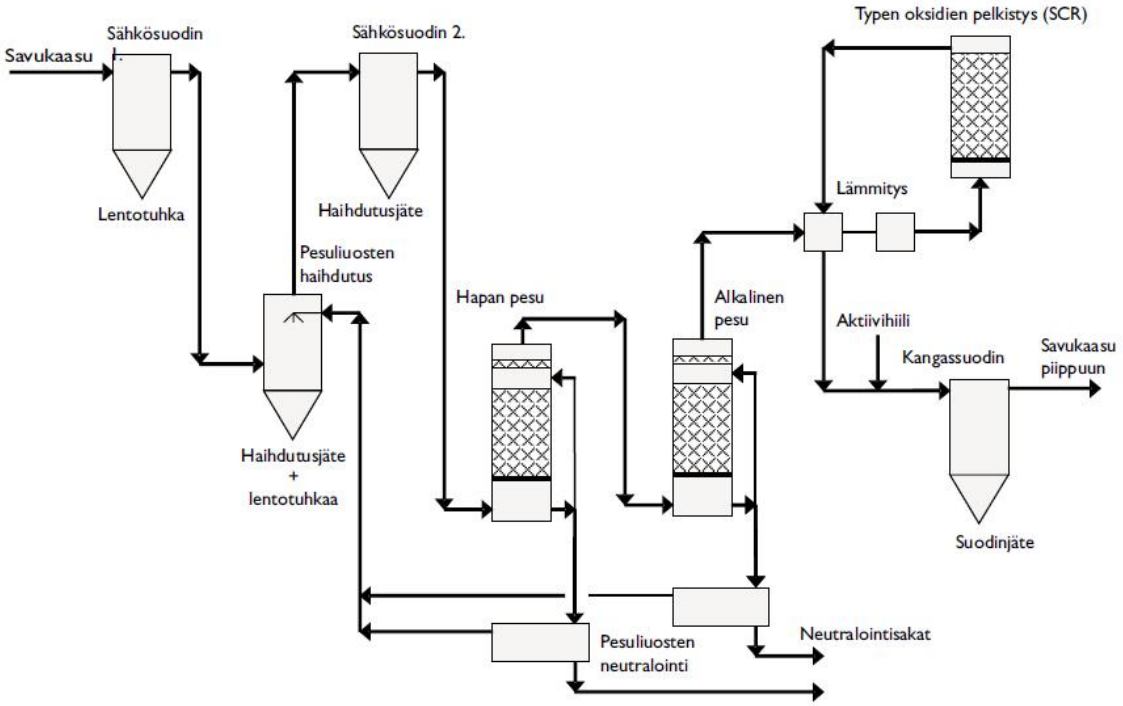


Figure 6.1. *Process flow chart of wet scrubber system of a typical large-scale waste incineration plant. (Jätteenpoltto BREF 2006, p. 37)*

It has been noticed that the plastic components that are used in wet scrubbers can act as intermediate PCDD/F storage. Two different operation models have been introduced; dioxins that are formed during unconventional operation (startups, when operated at partial load, during boiler trips) are absorbed in the plastic parts, from which they can be released little by little during a long period of time of normal operation. This is usually called as the "memory effect" in scrubbers. (Löthgren C.-J. & Bavel B. 2005) Dioxins may also be absorbed to the plastic parts during a long period of stable operation and reach a state of equilibrium between absorption and desorption. Since the adsorption/desorption balance is found to be highly temperature dependent, large loads of dioxins may be released to the surroundings during temperature peaks caused by unconventional operation. (Kreisz S. et al. 1996)

For the purpose of combating against the memory effect in the scrubbers, a special material has been developed. The plastic material, such as polypropylene, absorbs the dioxins as described above. After that, the dioxin molecules are diffused on carbon particles, which prevent them to be released during temperature peaks. The polypropylene protects the carbon species from other contaminants, such as mercury. This is found to offer a long-term reduction of PCDD/F emissions. (Götaverken Miljö AB 2013)

6.3 Bag house filters

Bag house filters (BHF) or fabric filters (FF) are used to collect particles from the flue gas. They consist of compartments containing a number of fabric bags. The flue gas

passes through the filter bags, which retain the particle stream to be passed to the clean side of the filter fabric. The particles attach to the surface of the bags and form a particle cake on the surface of the bags. The formed cake participates in the filtration process which increases the separation efficiency of the filters. The dust cake is removed regularly to a hopper by an air pulse or by a shaker to avoid excess pressure drop over the filter fabric and the dust cake, but simultaneously maintaining the filtration efficiency at a sufficient level. (Oksanen A. 2004, p. 4.39-4.43)

Bag house filters may also be used to remove unwanted gaseous emissions, such as SO_2, HCl, heavy metals, and PCDD/Fs from the flue gas, when operated together with dry sorbent injection. Common sorbents include sodium bicarbonate ($NaHCO_3$), hydrated lime ($Ca(OH)_2$), and activated carbon (AC). Sodium bicarbonate and hydrated carbon are used to capture SO_2 and HCl which are responsible of acid emissions, while the addition of activated carbon provides an effective reduction of heavy metals and PCDD/Fs. (Simatek 2012)

Bag house filters are primarily designed to reduce particle emissions. Therefore, the reduction efficiency is higher for solid phase than for vapor phase emissions. The temperature in which the BHF is operated may also play a vital role in the total PCDD/F emission in the stack. The temperature is likely to have effect both on the filtration efficiency and the possible formation of PCDD/Fs through de novo synthesis, which could take place in the dust cake on the filter fabrics. (Chi K. et al. 2006)

The partitioning between the solid and the vapor phase PCDD/F emissions was investigated at a conventional MSWI plant in terms of temperature variation. (Chi K. et al. 2006) The flue gas cleaning system involved a cyclone and a bag house filter with prior injection of activated carbon. The results proved that an optimal temperature for the PCDD/F reduction by a BHF and AC injection would exist and this would well below 200 ºC. Moreover, the reduction efficiency was higher for solid phase than for the gas phase PCDD/Fs. This investigation was followed by an experimental pilot-scale study which demonstrated that the filtration efficiency of gas phase dioxins is highly temperature-dependent. Thus, the lower the temperature, the higher cleaning efficiencies are supposed achieved.

6.4 Injection of activated carbon

Activated carbon is usually mixed in the flue gas before the bag house filter in purpose of removing heavy metal and PCDD/F emissions from the flue gas. The adsorption capabilities of different activated carbon species vary and temperature has significant effect on the adsorption efficiency of activated carbon; the temperature should be kept below 200 ºC to ensure sufficient reduction of gaseous heavy metals, such as mercury. (Simatek 2012)

In addition to the reducing effect on PCDD/F emissions, activated carbon may also act as a PCDD/F source at the temperature region of de novo synthesis (about 200 to 450 ºC), which is another reason for the lower operating temperature of the bag house

filter. (Lundin L. 2013) Additionally, other carbon species, such as bituminous coal, soot and charcoal, are reported to form PCDD/Fs. (Addink R. & Olie K. 1995) Despite the guideline of 200 ºC for AC-injection, the optimal operating temperature seems to be clearly below 200 ºC, when it comes to efficient reduction of dioxins. (Chi K. et al. 2006, p. 4)

It is also questioned whether the already-captured dioxins and furans on the filter surface could be released to the gas phase during special conditions, which could cause increased penetration of gas phase PCDD/Fs to the clean side of the filter. Most probably the adsorption/desorption process is a reversible process, the balance of which is governed by predominant circumstances, such as pressure, temperature and concentrations of different gas and particle phase compounds.

The reduction of PCDD/Fs by activated carbon is based on adsorption. The end-product is then removed from the process. Therefore the dioxin content of the filter ash should be monitored because it may contain large amounts of dioxins and treatment of the collected fly ash may induce additional costs. (Chang M. et al. 2004)

6.5 Catalysts

Dioxins and furans can be decomposed through oxidation at high temperatures to form carbon dioxide, water and HCl. The reaction (Tang H. 2003, p. 3) can be written as

$$C_{12}H_nCl_8 - nO_2 \rightarrow (n-4)H_2O + 12CO_2 + (8-n)HCl. \quad (13)$$

However, heat treatment of flue gases at high temperatures would require considerable amount of energy. The need for additional heating can be eliminated by using catalysts that will decrease the reaction temperature (A. J. Chandler & Associates Ltd. 2006, p. 74). The catalytic reduction is the only method that destroys the dioxins, not only transfer the problem elsewhere.

Selective catalytic reduction (SCR or DeNOx-catalyst) is a commonly used method for reducing nitrogen oxides (NO_x) from the flue gases. The flue gases travel through a honeycomb-shaped construction made of catalyst material, Ammonia, NH_3, that is injected in the flue gases, reacts with nitrogen oxides (NO or NO_2), thus producing water and molecular nitrogen (N_2). The process takes place at temperatures from about 250 to 400 ºC. The most common catalysts are vanadium oxide (V_2O_5) and wolfram oxide (WO_3). (Raiko R. et al. 2002, p. 332)

These catalysts are also found to promote the oxidative destruction of PCDD/Fs. (Hadzić A. 2010; A. J. Chandler & Associates Ltd. 2006, p. 75). Royal Dutch Shell Group has developed a product called Shell Dioxin Destruction System (SDDS) that is based on the same principals than conventional DeNOx-catalysts, but it is redesigned for more efficient destruction of PCDD/Fs. It is shown to remove efficiently (up to 99,9%) dioxins. The operating temperature is from 160 to 380 ºC, which allows placing

of the equipment in the clean side after other dust-collecting devices. The operation is possible without any or with only minor need for flue gas reheating. (Tang H. 2003)

Another catalytic method for destroying PCDD/Fs is a combination of fabric filtering and catalyst oxidation. This method involves propose-built filter fabrics covered with a catalytic layer. The filter fabric captures the particle phase pollutants, and the gas phase emissions travel through to the catalytic layer, where the dioxins are catalytically decomposed to carbon dioxide, water and HCl. A schematic picture of the process is shown in Figure 6.2. These types of filter fabrics are expensive compared to regular filter fabrics. Moreover, activated carbon injection cannot be used together with catalytic filters. (Simatek 2012; Bonte J. et al. 2001)

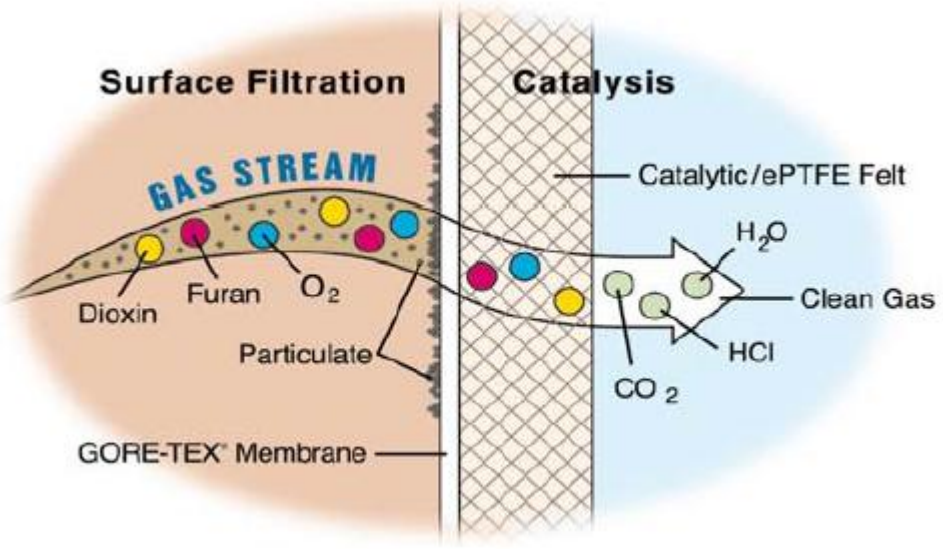


Figure 6.2. *Schematic picture of the combine effect of physical filtration and catalytic destruction of PCDD/Fs. (Bonte J. et al. 2001)*

6.6 Memory effect in flue gas channels

The “memory effect” is a term that is used to describe such situations, in which dioxins and furans or dioxin precursors are stored to a certain deposit or structure of the plant, and released during a long period of time, thus resulting in increased PCDD/F concentrations. The memory effect is usually connected to unconventional or unstable operation of the boiler, which may result from several factors.

The first possible form of the memory effect is related to incomplete combustion, which usually results from interruptions in use; boiler trips, irregular fuel feed, or operation at partial load, for instance, during start-ups and shutdowns. In this kind of situations, the combustion of the fuel is incomplete, which may result in increased level of dioxins, PICs, and residual carbon in the flue gas. These products are afterwards stored to fly ash deposits, from which dioxins can be released (desorption or de novo synthesis) during long period of time.

Another type of the memory effect is the already-presented (see Chapter 6.2) absorption-desorption-type memory effect that takes places in the wet scrubbers due to temperature variation. This phenomenon excludes the formation reactions of PCDD/Fs.

Wang L. et al. (2007) investigated the influence of start-ups on dioxin emissions in a municipal solid waste incinerator. The PCDD/F concentrations were found to be highly elevated even after 18 hours after the start-ups and the high PCDD/F emissions released due to the start-up was calculated to account for about 60% of the annual PCDD/F emission. This demonstrates the potential of unstable boiler operation on PCDD/F emissions.

Li H.-W. et al. (2011) carried out an experiment on the effect of aged fabric filters on PCDD/F emissions. A clear increase in the PCDD/F concentrations over the fabric filter was found. They concluded that dioxins may accumulate in the filter cake and be released in the gas phase later when the PCDD/F concentrations are lower. The tendency of different congeners to be released in the gas phase is influenced by the vapor pressure of each congener.

7 PCDD/F FORMATION AND FINGERPRINTS FROM DIFFERENT WASTE COMBUSTION PROCESSES

PCDD/F congener distributions are called as fingerprints because they can be used as a tool for defining the governing formation pathways of PCDD/Fs. In this chapter, the basics of the analysis will be introduced. Additionally, the fingerprints from conventional grate-fired waste incineration and from fluidized bed combustion of waste will be discussed in detail. After reading this chapter readers should have a basic idea how the PCDD/F fingerprints look like and what factors possibly have effect on their formation.

7.1 Definition of fingerprints

As described in Chapter 3, dioxins and furans consist of a grand variety of compounds depending on the number and position of chlorine atoms attached to the aromatic rings. In total, there are 210 different PCDD/F congeners. The name congener refers to compounds with similar characteristics and similar chemical structure. The congeners with same molecular formula are called isomers. Respectively, the groups of isomers are called homologues, thus, in total there are eight PCDD homologue groups and eight PCDF homologue groups (one to eight chlorine atoms attached to the benzene rings).

To visualize and to facilitate analysis of PCDD/F emissions, various congener, isomer, or homologue patterns (bar charts) may be formed. Since homologue patterns just tell the amount of congeners with same amount of chlorine atoms, they only offer information of the degree of chlorination. This may be useful information when the role of chlorination and dechlorination reactions and the effect of varying process parameters are considered.

Isomer and congener patterns include more information because they show the amount of individual congeners. Isomer patterns are found to be independent of combustion conditions, while homologue patterns are not (Iino F. et al. 2000, p. 4). Therefore, they can offer more specific details of the formation routes of PCDD/Fs. For this reason, isomer and congener patterns are called “fingerprints”.

Fingerprints can be used to determine possible precursors by comparing the PCDD/F fingerprints from a known compound or formation through a certain reaction, with the fingerprints from municipal waste incineration. For instance, the role of PCDD/F formation from chlorophenols in some process can be well investigated

because the fingerprints from different chlorophenols are available (Ryu J.-Y. 2005a, 2005b, 2006). Consideration of fingerprints may also offer valuable information of the significance of de novo synthesis or chlorination and dechlorination reactions during the process. It may also be used to define the routes in which the additives, such as sulfur, take effect by observing the existence of individual congeners. By comparing different fingerprints from municipal waste incinerators, fluidized bed incinerators, or other combustion processes, the investigation and the definition of governing formation routes should be possible.

The emission measurements reports from industrial power plants usually include the fingerprints of the 17 "dioxin-like" congeners that are responsible of the overall toxicity of the emission. Knowing the absolute amounts of those 17 congeners only offers information of the formation routes to a certain extent, if any, because information of the remaining 193 congeners is missing. Consequently, when the PCDD/F absolute concentrations (ng/m^{3}n) are expressed in toxic equivalents, the actual behavior of the PCDD/Fs remains unclear. In other words, if the toxic equivalent (given in ng/Nm^3 I-TEQ) increases between two different measurement points, the actual concentration of the dioxins may decrease, and vice versa, due to different toxic equivalent factors of the congeners (see Table 1.1). This may result from two things: First, the congeners that are detected at the first measurement point may transform to other congeners that are included in the 17 TEQ-congeners, but which have different toxicity equivalent factors. Alternatively, they may transform to other congeners than those included in the 17 TEQ-congeners, which simply removes them from the scope of TEQ calculations.

7.2 PCDD/F fingerprints from thermal industrial processes

Buekens A. with his co-workers (2000) analyzed data from various industrial processes, including metallurgical processes, cement kilns, and waste incinerators. The homologue patterns from the named processes were found to remind each others, as can be seen from the Figure 7.1. This proposes the idea that the governing formation pathways in all thermal processes are rather similar. However, dissimilarities can also be observed. This is likely due to differences in the process parameters of different processes; certain formation pathways and the production of certain congeners or homologues are favored over others.

The group of tetrachlorinated dibenzo-*p*-dioxins (TeCDD or T_4CDD) was found to be the most abundant group of dioxins in most of the cases, whereas the groups of tetra- to hexachlorinated congeners dominated among the furans. These homologue patterns include all dioxin and furan congeners. It is important to recognize that the amount of possible 4- to 6-chlorinated congeners is much higher than the amount of possible 7- and 8-chlorinated congeners.

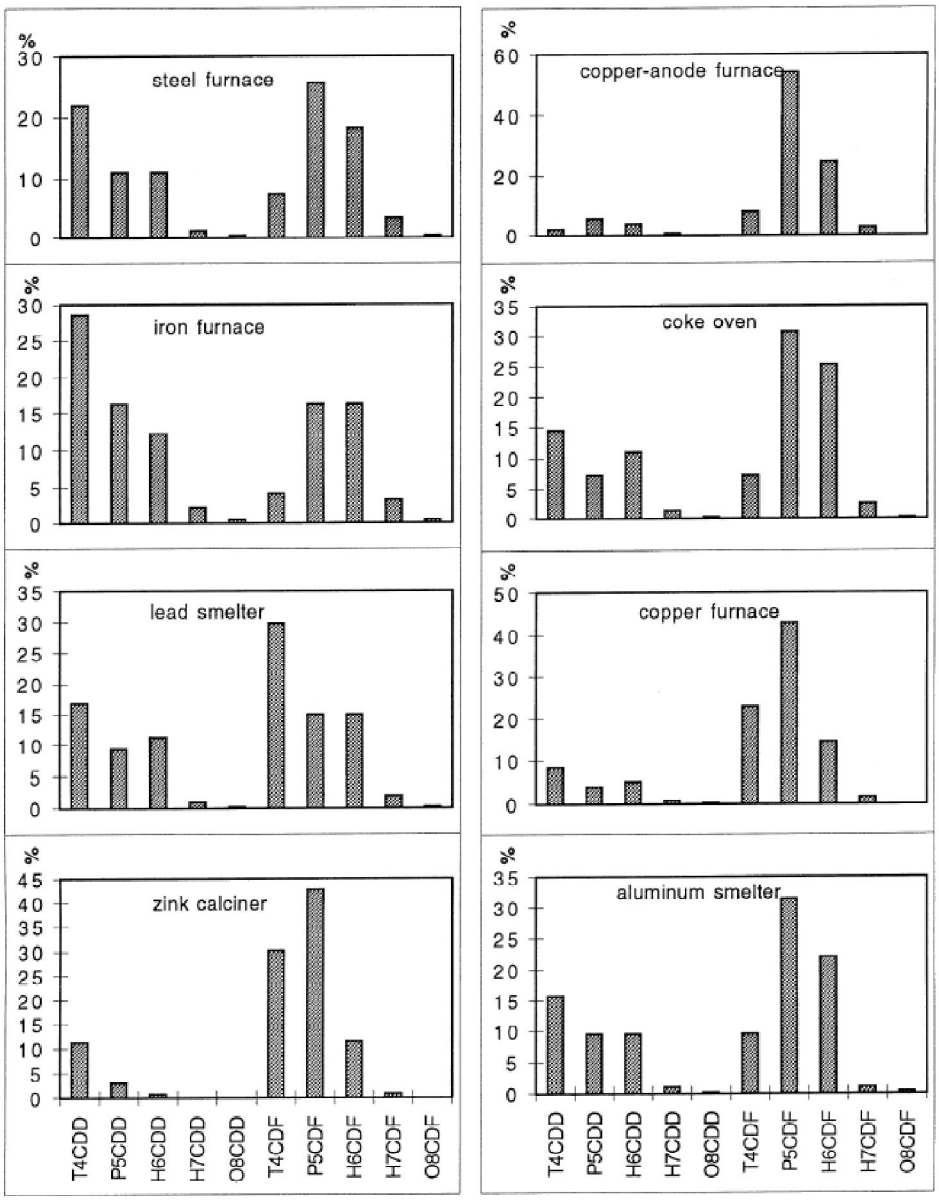


Figure 7.1. *Homologue distributions from various industrial processes. (Buekens A. et al. 2000, p. 3)*

Despite the similarities in the homologue patterns of different thermal processes, the congener patterns of 2,3,7,8-substituded congeners (I-TEQ congeners) were found to intensively vary. The I-TEQ pattern from aluminum plant (Figure 7.2), in which the 2,3,7,8,-chlorinated dibenzofuran clearly dominated, was completely different to those from a copper smelter (Figure 7.3). This observation proves that the PCDD/Fs are formed through different pathways in thermal processes with different process parameters and fuel properties. To be able to get decent results of the formation pathways, separate analysis of all congeners, not only the 2,3,7,8-substituded, would be essential.

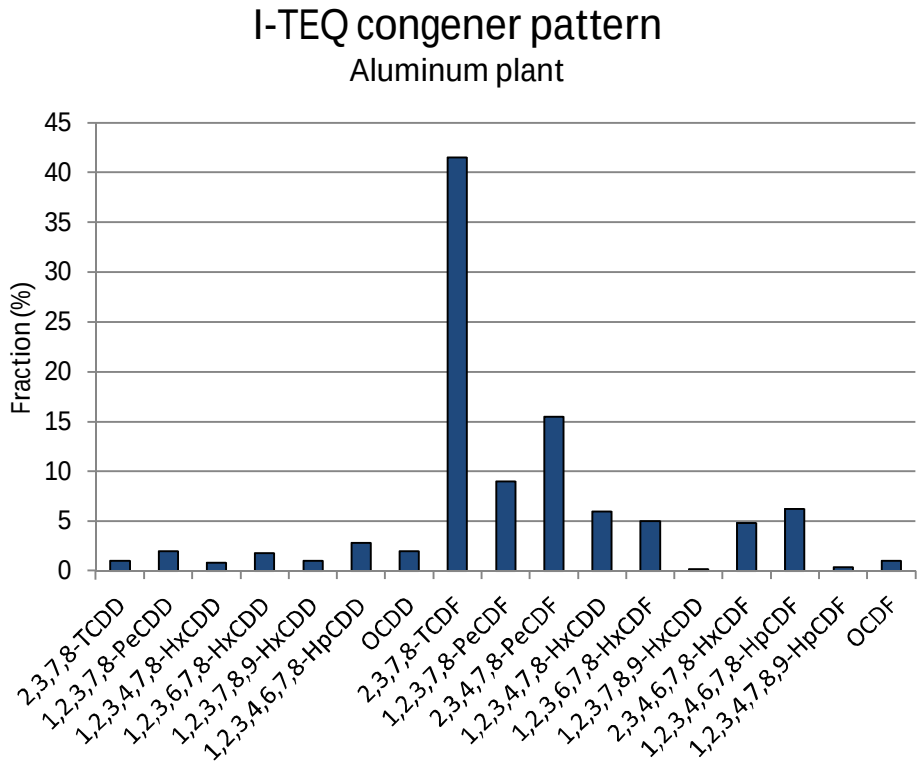


Figure 7.2. *I-TEQ congener pattern from an aluminum plant. (Buekens A. et al. 2000, p. 4)*

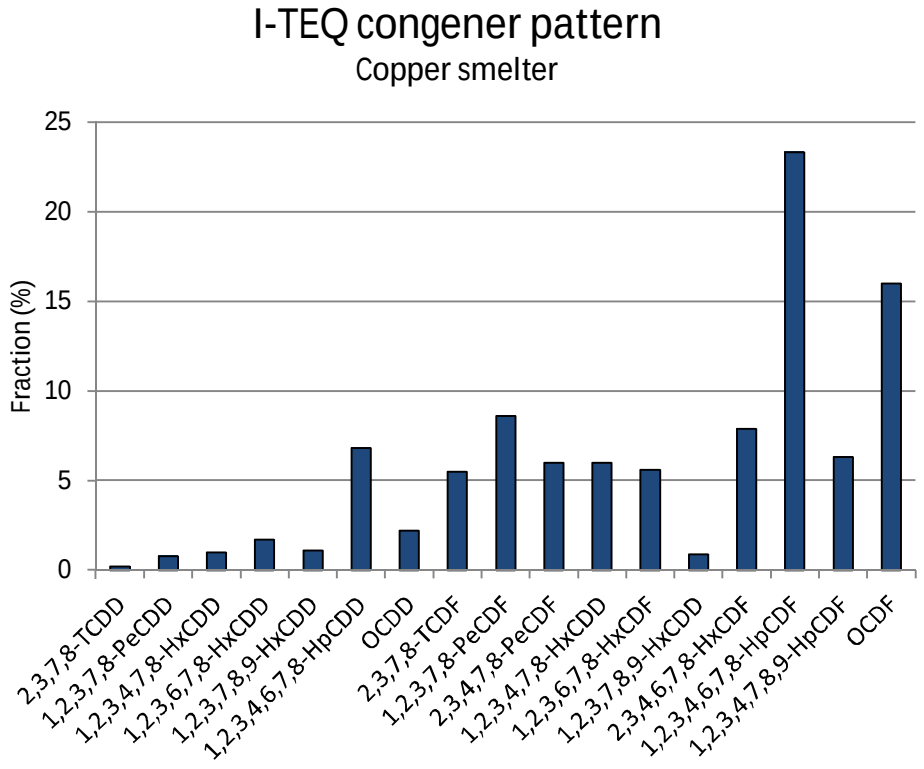


Figure 7.3. *I-TEQ congener pattern from a copper smelter. (Buekens A. et al. 2000, p.4)*

On the other hand, the I-TEQ pattern from the copper smelter (Figure 7.3) has great similarities with the I-TEQ pattern from municipal waste incinerators. This suggests that dioxins are formed via similar pathways in these two processes. Most probably the presence of copper, which sets the scene for catalyzed reactions, is the predominant factor in these cases. (Buekens A. et al. 2000) Fingerprints from MWIs will be discussed in the next Chapter 7.3.

7.3 PCDD/F fingerprints from grate-fired waste incinerators

Grate-fired boilers represent the most common type of incineration plant used in combustion of municipal solid waste (MSW). The benefits of a grate-fired boiler include low investment cost, lower power consumption, and almost non-existent need for waste fuel pre-treatment. For mainly these reasons, grate-fired boilers have held their position as the major waste incineration technology on the market.

The layout of a conventional grate-fired waste incineration plant is shown in Figure 7.4 below. The main elements of the plant include fuel receiving area, grate (stationary sloping, shaking or travelling grate), furnace, and boilers, which are followed by a combination of different air pollution control devices, such as ESP, BHF, and scrubbers.

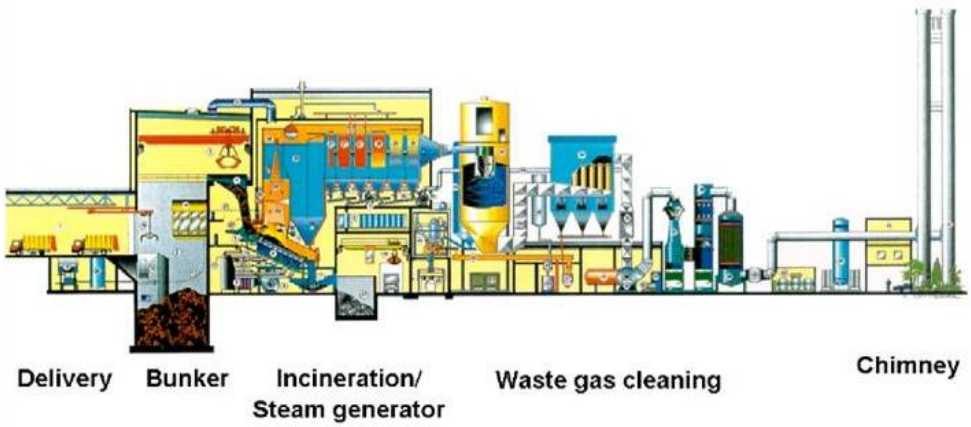


Figure 7.4. *A typical grate-fired waste incineration plant. (Waste Control 2013)*

The emissions from grate-fired boilers are more dependent on combustion conditions and fuel load variations than form FB boilers. (DeFusco J. 2007) More excess air is needed to allow sufficient combustion, which leads to higher primary NO_x emissions. Large particles in the fuel feed commonly cause blockages and unhomogenous fuel will cause fluctuation of the process conditions. In general, the emissions including the PCDD/Fs from grate-fired boilers are higher than from fluidized bed boilers, especially during start-ups and unstable operation. (Wang L.-C. 2007; DeFusco J. 2007)

The process parameters (e.g. temperature, residence times, fuel, O_2-level, fuel characteristics) are of the same magnitude both in grate-fired waste incineration and in fluidized bed combustion. Therefore, the fingerprints from municipal waste combustion using different technologies are basically very similar and the main formation routes that govern in waste combustion processes, including grate-fired waste incineration, hazardous waste incineration and fluidized bed combustion, are similar to a certain extent. The PCDD/F formation routes and fingerprints from traditional grate-fired waste incinerators will be discussed in this chapter.

7.3.1 PCDD/F homologue distributions from grate-fired boilers

The homologue distributions from municipal waste incinerators are usually a bit different compared to the homologue distributions presented earlier in Figure 7.1. Ryu J.-Y. et al. (2004) analyzed a number of samples from several stoker-type MSWI flue gases. The average homologue distribution of dioxins and furans for all 8 homologue groups (mono- to octa-) can be seen in Figures 7.5 and 7.6 below. Hexa- and heptachlorinated congeners were found to dominate among the dioxins, while lower chlorinated congeners are present in lower amounts. The major group among the furans was the group of trichlorinated isomers.

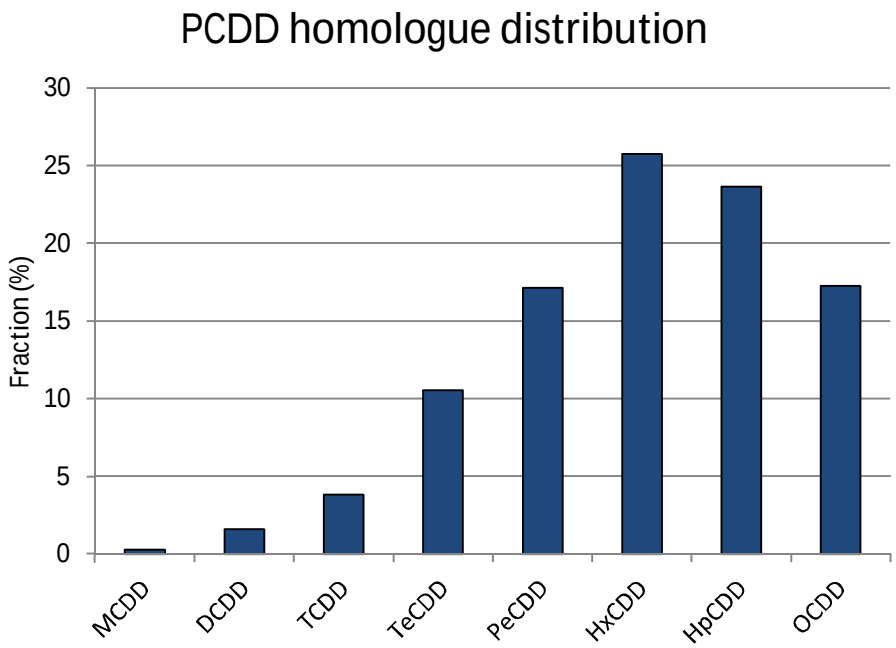


Figure 7.5. *PCDD homologue distributions of MSWIs. (Ryu J.-Y. et al. 2004, p. 4)*

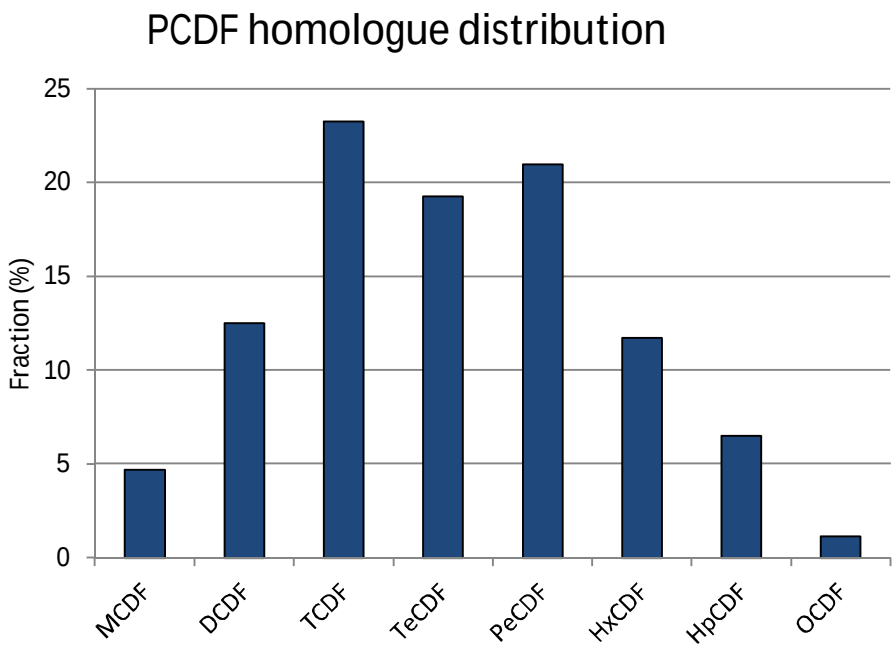


Figure 7.6. *PCDF homologue distributions of MSWIs. (Ryu J.-Y. et al. 2004, p. 4)*

7.3.2 PCDD/F fingerprints form grate-fired boilers

A typical I-TEQ congener pattern (2,3,7,8-substituted congeners) from municipal solid waste incineration can be seen in Figure 7.7. This congener pattern is the average of four different municipal waste incinerators (stoker type) in northern Spain.

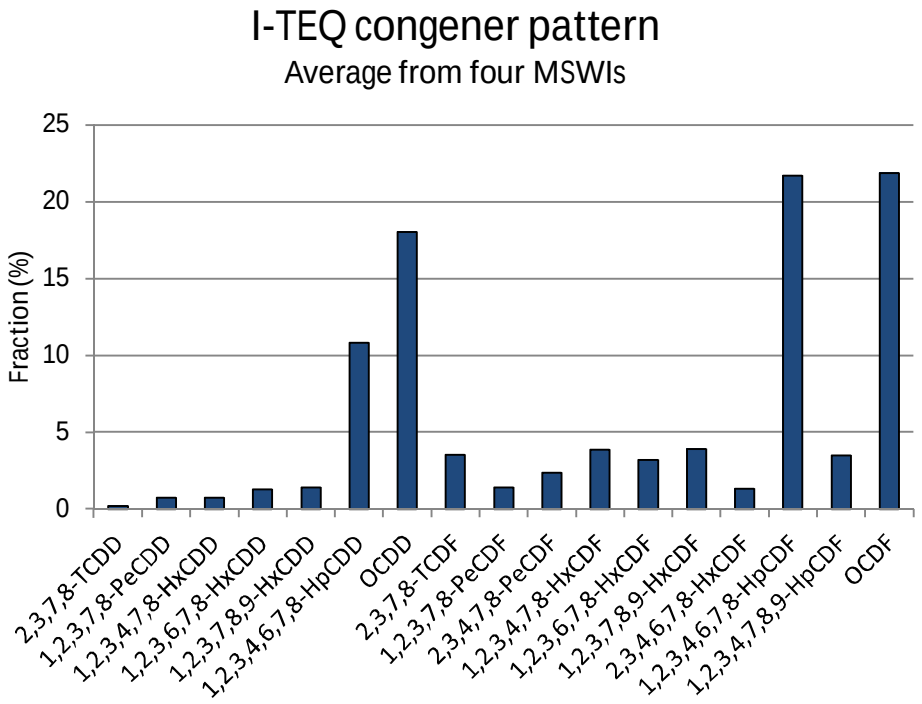


Figure 7.7. *A typical I-TEQ congener pattern from MSWI stack gases. (Abad E. et al. 1997)*

Very similar profiles are found in hazardous waste incinerators and medical waste incinerators, shown in Figure 7.8 below. (Cleverly D. et al. 1997) The influence of air pollution control devices (APCD) must be considered, because these congener patterns are measured from the stack. 1,2,3,4,6,7,8-HpCDD and OCDD clearly dominate among the dioxins. 1,2,3,4,7,8-HxCDF , 1,2,3,4,6,7,8-HpCDF and OCDF are the most abundant congeners of furans.

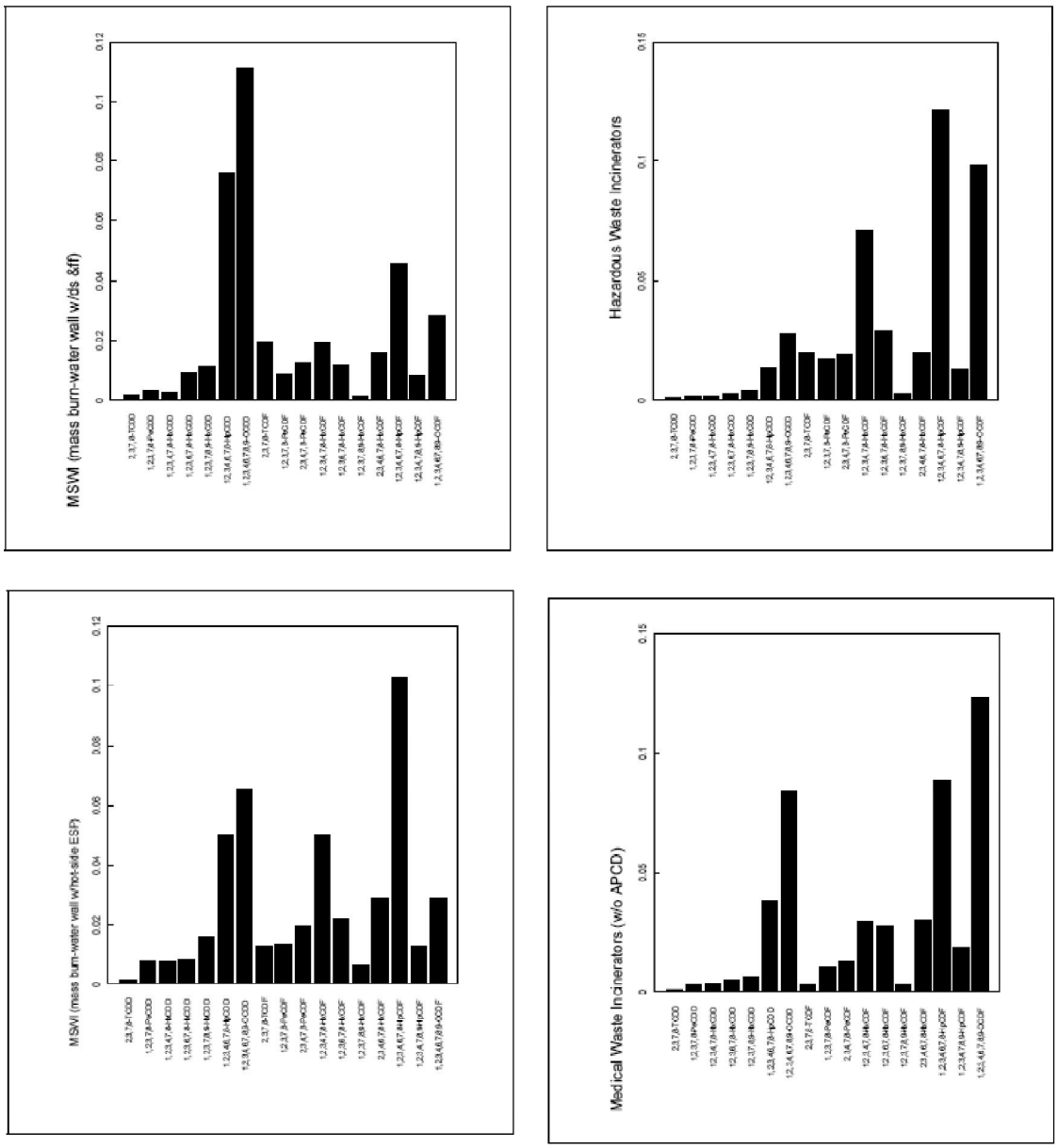


Figure 7.8. *I-TEQ congener patterns from various types of waste incinerators. (Cleverly D. et al. 1997)*

These profiles, however, only contain a limited amount of information of the formation pathway because only seventeen congeners of the 210 possible congeners are

represented. For that reason, we will now take a closer look to the full congener patterns from MSWIs.

7.3.3 Determination of formation pathways from PCDD/F fingerprints

Ryu J.-Y. et al. have been investigating different PCDD/F formation pathways, such as chlorination pathways (2004), condensation of phenol precursors (2005b), and $CuCl_2$-catalyzed reactions (2005a), by analyzing the complete homologue and isomer distributions of PCDD/Fs. In purpose of defining the governing formation pathways of PCDD/F formation, they carried out an extensive experiment (Ryu J.-Y. et al. 2006) which included in-depth comparison of data from municipal waste incinerators, including several grate and FB boilers, and data from laboratory-scale MSW combustion tests. The data from MSWIs were compared with the patterns from laboratory-scale tests of $CuCl_2$-catalyzed and gas phase condensation of phenols, and with computational models of chlorination (from DD and DF) and dechlorination (from OCDD and OCDF) patterns.

The results from this experiment were encouraging. As an example, the isomer pattern for tetrachlorinated dibenzo-p-dioxins is presented in the Figure 7.9 below.

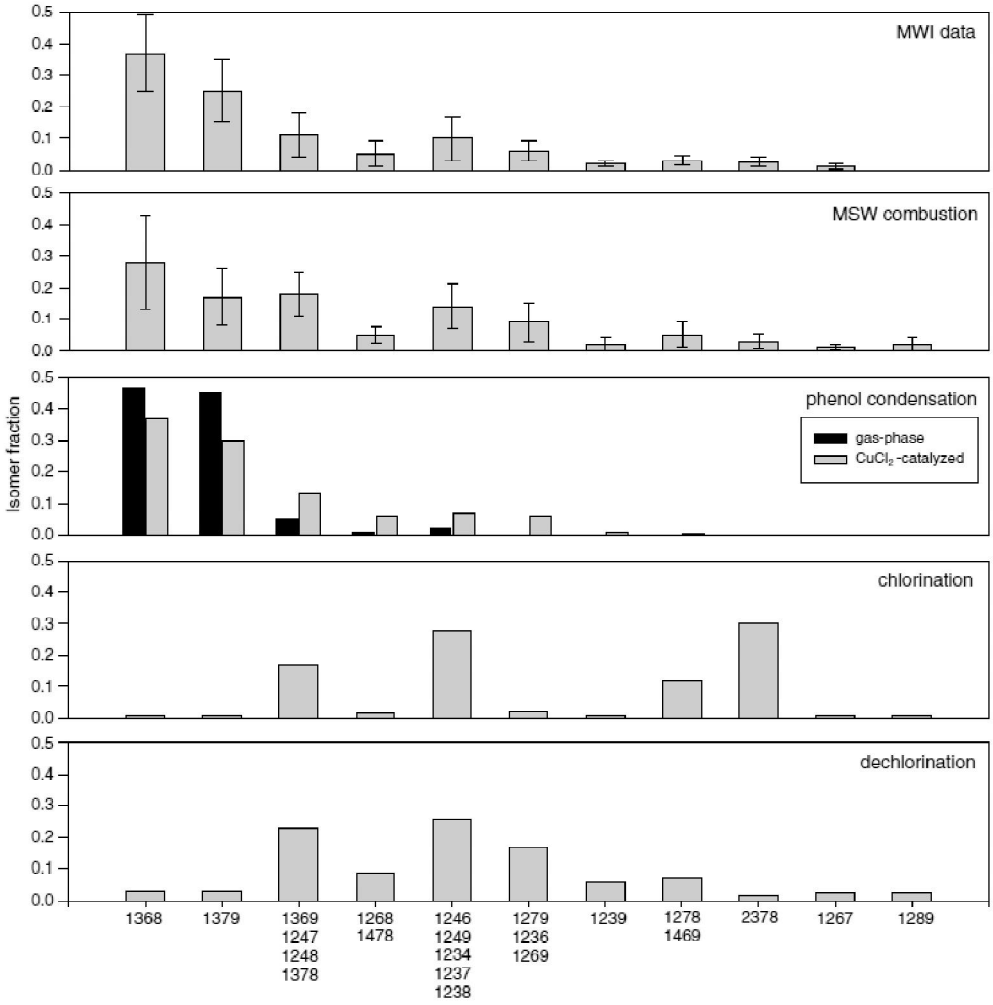


Figure 7.9. *Isomer pattern of tetrachlorinated dibenzo-p-dioxins. (Ryu J.-Y. et al 2006)*

As it can be seen, the isomer profile of TeCDD from large-scale municipal waste incinerators, experimental MSW combustion results, and the profiles from condensation of chlorinated phenols show remarkable similarity. From this result it may be at least supposed, that the formation of tetrachlorinated dibenzo-p-dioxins is governed by condensation of phenol precursors. Moreover, the isomer pattern from field incinerators and lab-scale tests seem to correlate well, indicating that relatively good results may be obtained from laboratory-scale tests. (Ryu J.-Y. et al. 2006)

The study (Ryu J-.Y. et al. 2006) included also similar comparison for other isomer patterns of tetra- to hexachlorinated dioxins and furans. The results indicated that the formation of tetra- and pentachlorinated dioxins would be governed both by the gas phase and $CuCl_2$-catalyzed formation from chlorinated phenols; more precisely from 2,4,6-TCP, 2,3,4,6-TeCP and PCP, which are found to be abundant in MSWI flue gases. (Mulholland J. & Ryu J.-Y. 2001) The formation of hexachlorinated dioxins would be mainly governed by $CuCl_2$-catalyzed phenol condensation and dechlorination from octachlorinated dibenzo-*p*-dioxins (OCDD).

Respectively, the formation of lower chlorinated furans (mono- to tetrachlorinated) was found to be governed by chlorination of dibenzofurans (DF), whereas the formation of higher chlorinated furans was found to be governed by dechlorination of OCDF. Chlorination and dechlorination reactions are believed to occur simultaneously. The 'R value', which represents the correspondence between the models and measured values, reached relatively high values from about 0.56 up to 0.99, the latter of which was obtained for $CuCl_2$-catalyzed condensation of phenols. (Ryu J.-Y et al. 2006) The concentration of dibenzofurans (DF) in the flue gas of MSWIs is found to be substantially higher than the total concentration of total PCDFs. Also, the concentration of dibenzofurans is found to significantly reduce in the convective section of the MSWI. (Wikström & Marklund 2000, see Ryu J.-Y. et al. 2004) These findings indicate that the chlorination of DF into PCDFs may play an important role in municipal waste incinerators. (Yamamoto T. et al. 1989, see Ryu J.-Y. et al 2004)

Similar results have been obtained by Iino F. et al. (2000). It may be assumed that the above-mentioned formation pathways are the ones that most likely dominate in municipal solid waste incinerators and in other waste combustion processes. Corresponding comprehensive analysis, and comparison between the fingerprints from laboratory-scale tests and large-scale power plants, is required in order to obtain enough information for determination of the PCDD//F formation pathways in thermal processes.

7.4 PCDD/F fingerprints from fluidized bed boilers

Fluidized bed combustion is a competing technology for grate-fired waste incineration. Fluidized bed combustion can be divided in two major technologies; bubbling fluidized bed (BFB) combustion and circulating fluidized bed (CFB) combustion. These technologies and PCDD/F emissions from FB boilers will be introduced in this chapter.

The overall process of traditional grate-fired waste incinerators and modern fluidized bed boiler plants only varies little, although, a number of minor differences between these boiler types exist. The aim of this chapter is to find out the important differences between grate-fired boilers and fluidized bed boilers, which may have effect on PCDD/F emissions.

7.4.1 Bubbling fluidized bed boilers

Bubbling fluidized bed (BFB) combustion is a technology that is commonly used for firing mainly different types of biomass (bark, forest residues, saw dust, peat, agro fuels, sludge) and waste fuels (industrial and municipal waste). The fuel is fed into the sand bed (Figure 7.10) that is fluidized by upwards flowing fluidizing gas consisting of primary air and recirculation gas. The volatile fraction of the fuel evaporates and is combusted in the upper furnace supported by secondary and tertiary air feeding. Solid char that remains in the fluidized bed will burn inside the fluidized bed and the remaining unburned material (bottom ash) is removed from the bottom of the furnace. The primary air flow is low enough to avoid the bed material exiting the furnace.

Figure 7.10. *Bubbling fluidized bed boiler. (Metso Power Oy 2012)*

7.4.1.1 Fuel, combustion zone conditions and fly ash

One major difference of FB boilers in general compared to grate boilers is the need for fuel pre-treatment. The fuel in FB boilers must be sorted and crushed to smaller particle sizes. As it may be expected, fuel pre-treatment automatically increases the costs of the plant, but it has remarkable benefits on the quality of the combustion process. The primary air will reach the fuel particles easily and more complete combustion is achieved. This reduces the amount of unburned content in the bottom ash, which can be relatively high in bottom ashes from a grate-fired boiler. (DeFusco J. et al. 2007)

The amount of bottom ash in grate-fired boiler is high, about 35 to 70 %. (DeFusco J. 2007) In contrast, the amount of bottom ash in BFB boilers is very low; in general, more than 90% of the ash is present as fly ash that is entrained from the furnace by the flue gas stream and collected by dust-collecting devices. (Metso Power Oy, 2012) The high amount of fly ash in the post-furnace zone of BFB boilers may create favorable circumstances for PCDD/F formation, which could possibly be the major reason for higher PCDD/F emission in some particular BFB boiler plants.

The temperature profile of BFB boilers is little bit different than the profile of grate boilers. The bed temperature is kept rather constant at about 850 ºC and the highest temperatures (1000 to 1100 ºC) are reached at the secondary air level. After the secondary air level, the temperature decreases linearly with the furnace height. (Metso Power Oy, 2012) Due to large mass of the hot sand bed, the operation of the process is more stable compared to grate-fired boilers. This evens the emissions peaks during changes in the fuel characteristics. (DeFusco J. et al. 2007) The temperatures can be maintained relatively well above 850 ºC after tertiary level when operating at 70 to 100 % load and the requirement of 2 seconds will be achieved. When operating at lower loads (<50%), the temperature may not be sufficient to reach these requirements and higher emissions, including PCDD/F emissions, are expected.

7.4.1.2 PCDD/F fingerprints from BFB boilers

An average PCDD/F I-TEQ fingerprint from a BFB boiler using MSW and biomass as fuel is shown in Figure 7.11. As it may be observed, it is extremely similar to the fingerprint from grate-fired waste incinerators. Therefore, it can be partly concluded that the PCDD/Fs are mainly formed through similar pathways both in grate-fired and in BFB boiler plants. The amount of furans is considerably higher than the amount of dioxins, which suggests that de novo synthesis play a significant role. The abundance of higher chlorinated congeners indicates of presence of copper catalysts which promotes chlorination of lower chlorinated congeners towards the octachlorinated ones. The small amount of the 1,9-substituded congeners may be explained by the order of chlorination through electrophilic substitution and the thermodynamic instability of this congener. The 1,9-substituted congeners are found in lower amounts in grate-fired boilers. Instead, only some 1,9-substituded congeners are found in lower amounts in FB boilers. The production of those congeners is found to be impossible via condensation of chlorophenol with chlorobenzene congeners that are found in large amounts in FB

boilers. This suggests that condensation of phenols and benzenes play a key role in FB boilers. (Weber & Hagenmaier 1999b)

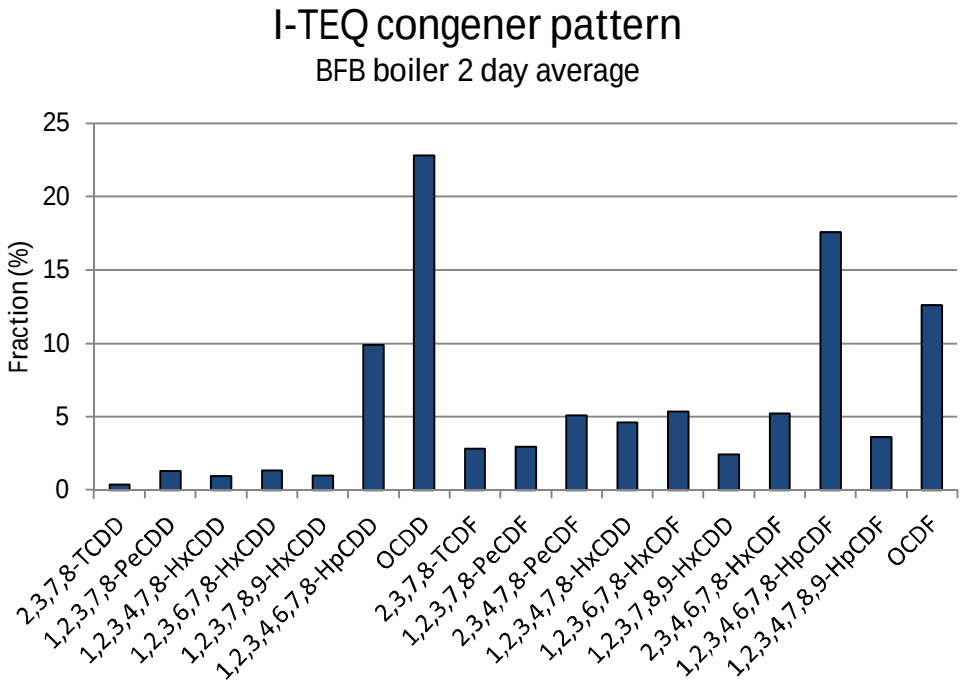


Figure 7.11. *I-TEQ congener pattern from BFB boiler. (Metso Power Oy)*

Weber & Hagenmaier (1999b) carried out a profound analysis on complete PCDD/F fingerprints from several stoker-type grate-fired MSW incinerators and FB boilers combusting waste in order to find out the differences between these two boiler types and to find out the possible reasons for the differences. The congener distributions from grate-fired boilers were found to consist of almost all possible congeners in comparable amounts, while the distributions from FB boilers were dominated by certain congeners. As a result, the congener pattern form fluidized bed boilers were found to lead to minor production of 2,3,7,8-TeCDD and 1,2,3,7,8-PeCDD, and therefore furans account for over 80% of the total I-TEQ in FB boilers. The homologue profile of furans showed that in FB boilers the HpCDF are the most abundant, whereas the groups of tetra- and pentachlorinated furans dominate in grate-fired boilers. (Weber & Hagenmaier 1999b, p. 6) However, if we look the figures 7.7 and 7.11, we may see that the congener distributions of the 2,3,7,8-substituted congeners are highly similar from the case MSWI boilers than from the case BFB boilers. To see if the earlier findings by Weber & Hagenmaier (1999b) coincide with these patterns, a full fingerprint pattern of all PCDD/F congeners would be needed.

Three major formation pathways were considered in the analysis; condensation of intermediates (precursor mechanism), formation from carbon backbone structure (de novo synthesis) and chlorination/dechlorination reactions. The formation of PCDDs could be completely explained by the condensation of the most abundant precursors; 2,4-, 2,4,6-, 2,3,4,6-, and pentachlorinated phenol. These were found both in the gas

phase and in the fly ash, and they were responsible of about 90% of the total chlorophenols in FB boilers. A clear correlation between the concentration of PCDD and CPhs in the fly ashes was found, suggesting that fly ash -catalyzed formation from chlorinated phenols plays the major role in PCDD/F formation. Formation through chlorination/dechlorination reactions and de novo synthesis were suggested to play a minor role, although it is usually considered as the major formation pathway of PCDD/Fs. Both processes occur simultaneously at same part of the flue gas channels, though it may be difficult to define which formation route dominates at a certain plant. (Weber & Hagenmaier 1999b, p. 6-7)

While the formation of PCDDs was governed by condensation of chlorophenols, the formation PCDFs was found to be governed by condensation of chlorinated phenols and chlorinated benzenes. The combination of the most abundant chlorophenols (2,4-, 2,3,4-, 1,2,4-, and 1,2,3,4-) and chlorobenzenes (1,2,3-, 1,2,3,4-, PCP) lead directly to the most abundant PCDF congeners. All these differences in PCDD and PCDF patterns were suggested to be caused by high calcium content in the fly ashes, which result from injection of $CaCO_3$ into the furnace in FB boiler plants, or from injection of $Ca(OH)_2$ in the flue gases at around 350 degrees of Celsius. (Weber R. & Hagenmaier H. 1999b, p. 9)

Some interesting dissimilarities between the PCDD/F fingerprints from stoker-type grate boilers and FB boilers have also been observed by Weber R. et al. (2001). They concluded that especially furans would be formed via degradation of polycyclic aromatic compounds (de novo of PAHs), and a perylene structure in soot particles would be an important precursor, thus generating the difference in the fingerprints compared to those from grate boilers. High amount of fly ash, high calcium and heavy metal concentrations of the fly ash, and different soot formation behavior in FB boilers were suggested as the key reasons for the differences between grate-fired and FB boilers.

7.4.2 Circulating fluidized bed boilers

In circulating fluidized bed boilers (Figure 7.12) the amount and velocity of fluidizing air from the furnace bottom is higher compared to BFB boilers. Therefore, the fluidizing sand bed is entrained by the air out of the furnace to a cyclone separator, in which the fluidizing sand is separated from the flue gases and returned to the furnace through a loop seal. The flue gas continues to the convective section and is cleaned by flue gas cleaning equipment. CFB boilers are commonly used for combusting different biomass (including recycled wood), SRF, coal, and peat.

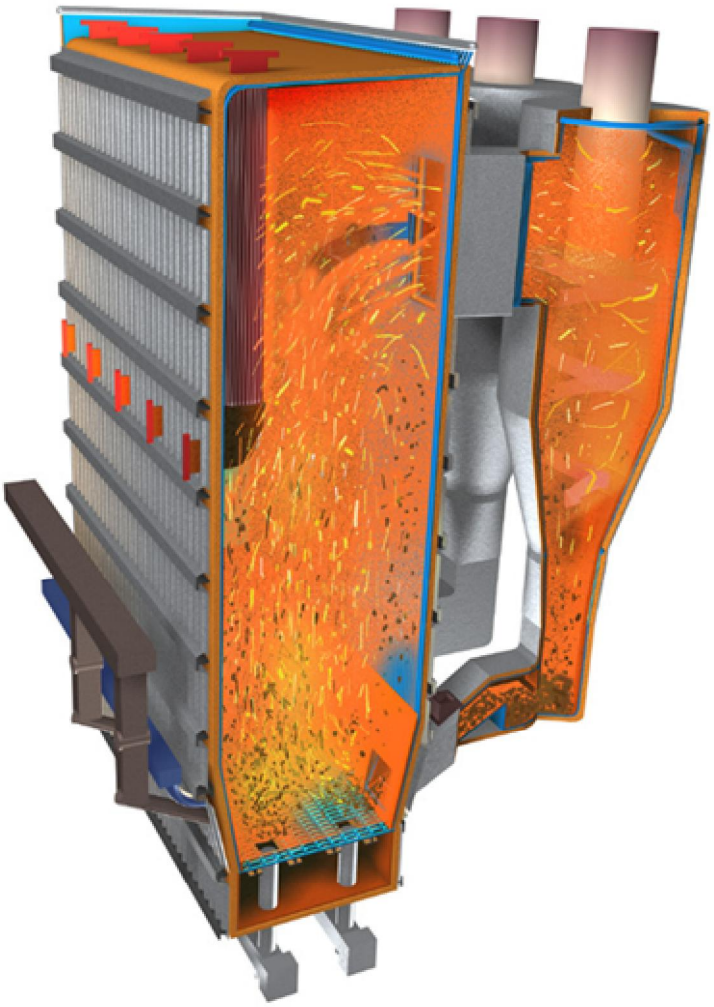


Figure 7.12. *Circulating fluidized bed boiler. (Metso Power Oy 2012)*

7.4.2.1 Fuel, combustion zone conditions and fly ash

The temperature in the furnace differs from the temperature profile of a bubbling fluidized bed boiler. High temperatures (>1000 ºC) are usually not reached and the temperature is very even from the furnace bottom until the furnace exit at full loads. The requirement of 2 seconds above 850 ºC will be achieved because the temperature may remain above 850 ºC also in the cyclone separator. However, at lower loads (<40%) the temperature decreases remarkably leading to high possibility of too short residence time above 850 ºC. In general, the combustion process in CFB boiler is more efficient than in a BFB or grate-fired boiler due to good mixing of the fuel and combustion air, leading to very low emissions.

CFB boilers are usually equipped with limestone injection and SNCR (injection of ammonia or urea) in order to decrease SO_2 and NO_X emissions. This may have significant effect on the PCDD/F fingerprints from CFB boilers, as described by Weber R. & Hagenmaier H. (1999b). The pH of the fly ashes increases as alkaline compounds are injected into the process. This will likely affect the formation routes and inhibit the

formation of several PCDD/F congeners, which is possibly the key reason for differences between the PCDD/F fingerprints from grate-fired, BFB and CFB boilers.

Another difference between the CFB and BFB boilers is the amount and characteristics of the fly ash. In CFB boilers, the fly ash that exits the cyclone separator generally has smaller mean particle size than the fly ash from BFB boilers. Basically, the actual particle size distribution depends on the efficiency of the cyclone. Due to smaller dust particle size, the active surface of the fly ash (per kg of fly ash) is higher in CFB boilers compared to BFB boilers. The reactions in PCDD/F formation are suggested to be similar than in case of BFB boiler, but they may occur more rapidly and the possibility of PCDD/F formation significantly increases. (Lundin L. 2013) This also increases possibility of desorption of particle phase PCDD/Fs into the gas phase, which may lead to higher probability of PCDD/Fs penetrating the flue gas cleaning section. (Mätzing H. et al. 2001)

7.4.2.2 PCDD/F fingerprints from CFB boilers

I-TEQ congener pattern from a circulating fluidized bed boiler combusting SRF and recycled wood may be seen in the Figure 7.13. The basic shapes of the distribution pattern looks rather similar to those from grate-fired and BFB boilers (Figures 7.7 and 7.11). However, the dominance of certain congeners is clearer than in other boiler types. These results will be analyzed in detail in the next Chapter 8 and 9.

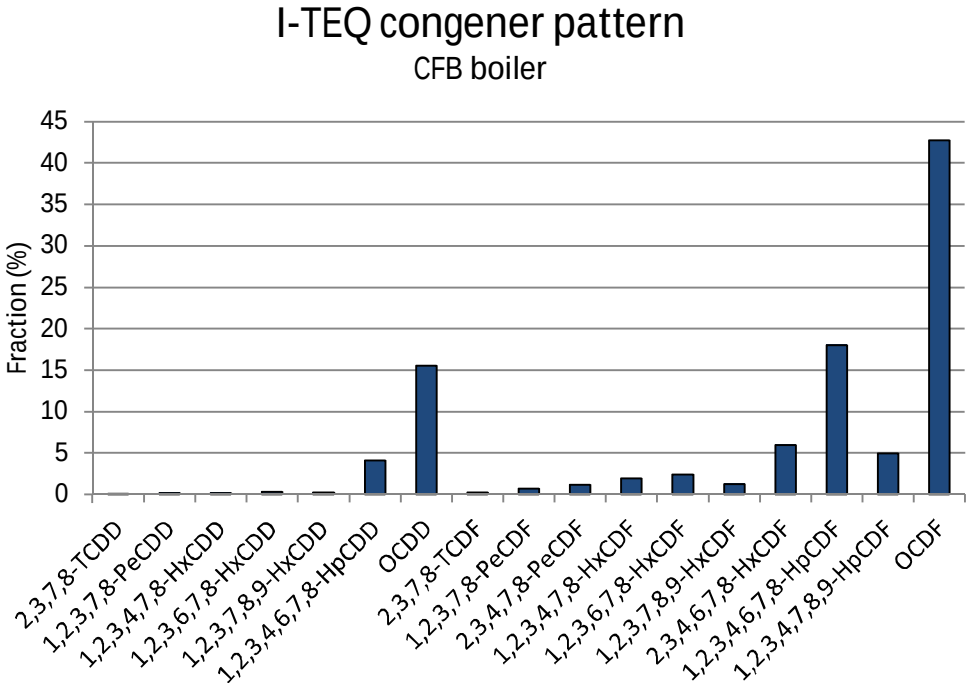


Figure 7.13. *I-TEQ congener pattern from a CFB boiler (Metso Power Oy)*

8 CASE 1: MEASUREMENT CAMPAIGN AT CFB BOILER PLANT

This chapter is the first one of the two chapters which will constitute the experimental part of the thesis work. Both of these chapters consist of short description of the projects and analysis of the results of measurement campaigns that are recently carried out at fluidized bed boiler plants delivered by Metso Power. PCDD/F emission measurements were included in both measurement campaigns in order to define the efficiency of flue gas cleaning equipment in these particular plants. In this chapter, we will focus on PCDD/F emissions from a CFB boiler. The results of this chapter will be later compared with the result from Chapter 9 in order to find out the major differences of the PCDD/F emissions between the BFB and CFB boiler plants included in the experimental part of the thesis work.

8.1 Definition of the project

A measurement campaign was carried out in 2012 at a Metso CFB boiler plant in order to gather information of the predominant circumstances in the boiler. As a part of this extensive measurement campaign, emissions including PCDD/Fs were measured at different locations of the flue gas channels during two measurement days.

8.1.1 Description of the boiler plant

The main part of the plant is the 125 MW_{th} (45 kg/s, 60 bar, 475 ºC) CFB boiler. The plant uses recycled wood (RW), solid recovered fuel (SRF) and coal (reserve) as fuel. The RW proportion in the fuel is typically from about 20 to 50%. The furnace is equipped with limestone injection (SO_2 reduction) and urea is injected at the cyclone inlet of the two cyclone separators (SNCR). After cooling in the empty pass and in the superheater and eco area, the flue gas is cleaned by an ESP (dust pre-collector), a bag house filter with prior injection of sodium bicarbonate and activated carbon, and a sodium hydroxide (NaOH) scrubber.

8.1.2 Fuel and additives during the measurements

On the 1st dioxin measurement day the fuel ratio was about 30/70 (RW/SRF) and on the 2nd day about 40/60. The fuel consisted chlorine from about 0.5 to 1.5 %-Cl by mass, which is clearly below the typical Cl-content of MSW reported by Kanters M. et al. (1996). This, however, is enough chlorine in fuel to allow significant formation of

PCDD/Fs. The chlorine content of the fuel in this particular plant is shown to correlate with the dioxin emissions to a certain extent. The net calorific value of the fuel was about 20 MJ/kg,$_{dry}$, and moisture of the fuel approximately 22%-w.

The content of copper in the fuel samples varies intensively due to unhomogenous distribution of metal species in the fuel mixture. The values of the Cu-content vary in range of 33 to 2700 mg/kg,$_{dry}$. Therefore, a correlation between the PCDD/F emissions and Cu-content of fuel samples is somewhat impossible to generate. The average Cu-content of the whole measurement campaign was 575 mg/kg,$_{dry}$ (0.0058%-w), which seems to be sufficient for PCDD/F formation and coincides with previous findings (Hatanaka T. et al. 2003, p. 3). The amount of chlorine and copper at a specific moment is difficult to predict and determine and they vary from day to day.

During the measurements, the feeding of $CaCO_3$ was shut down. On the 2nd day, sulfur was fed into the furnace by using the $CaCO_3$ feeding device. The urea feeding rate was constant on both days. The amount of sodium bicarbonate ($NaHCO_3$) was remarkably higher on the 2nd day due to higher amount of sulfur in the flue gases. The feeding rate of activated carbon was kept rather constant.

8.1.3 Boiler operation and flue gas temperatures

The process was rather stable on both days. On the first day, the temperatures of the cyclones increased due to minor problems with the bottom ash removal. On the second day, the temperatures in the left side of the furnace temporarily decrease, which may have an effect on the PCDD/F formation. The average process parameters were similar on both days, allowing a better comparison between the results of the two dioxin measurement days.

The essential information of the temperatures can be seen from the Table 8.1 below. The results show that no major differences between the two days can be observed. The bed temperature was little bit higher on the 1st measurement day, and the flue gas temperatures after the cyclone were slightly higher on the day 2.

Table 8.1. *Daily average flue gas temperatures at different locations of the boiler.*

Location	Unit	Day 1	Day 2
Bed	ºC	829	817
Furnace top	ºC	883	882
Cyclone out	ºC	919	923
Before ECO	ºC	344	352
Before ESP	ºC	166	169
Before BHF	ºC	164	167

8.2 Measurement of PCDD/Fs

The measurement of PCDD/F emissions from flue gases will be introduced in this chapter. This will include introduction of the sampling method and sample analysis,

description of the sampling points used in this measurement campaign, and possible problems that are encountered in PCDD/F emission measurements in general.

8.2.1 Measurement standard EN-1948 and PCDD/F sampling

In Europe, PCDD/F measurements are carried out according to standard EN-1948-1. This standard defines the minimum requirements for adequate measurement procedure in order to get reliable results. (S/EN1948-1/2006)

Before the measurement, all the parts of the measurement equipment will be rinsed with acetone and toluene in purpose of securing the cleanliness of the equipment. The equipment should be also cleaned between two measurements, however, in practice this is not always considered as necessary operation. Control blanks are taken in order to define the background concentration. The standard EN-1948-1 defines three possible methods, all of which can be used for PCDD/F sampling according to the standard; cooled probe method, dilution method and filter/condenser method. (S/EN1948-1/2006, p. 8)

In this case, the cooled probe method presented in Figure 8.1. was used. The flue gas sample is sucked isokinetically from the flue gas channel through a nozzle and a probe, in which the flue gas is cooled below 20 ºC. Some PCDD/Fs are condensed to the walls of the condensate flask, after which the gas enters impingers or solid adsorbents. Usually, a XAD-2 resin is used as solid adsorbent. After the final adsorbent, there is a filter, on which the solid phase PCDD/Fs are captured.

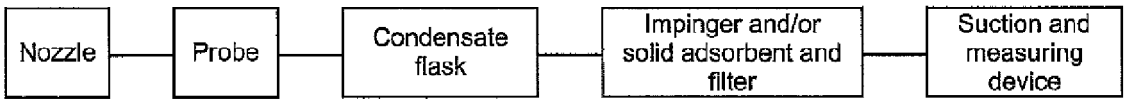


Figure 8.1. *Schematic representation of the cooled probe method. (S/EN1948-1/2006, p. 14)*

Samples from different parts of the measurement are analyzed in laboratory using gas chromatograph and high frequency mass spectrometer. (S/EN1948-1/2006; Mroueh U.-M. et al. 1988).

XAD-2 resin is a general adsorbent used in sampling of organic compounds. It has been observed that minor chemical and physical transformation reactions, including migration and cracking of the resin, may occur during the sampling. This might cause inaccuracy if the sample is contaminated by impurities that are remained in the resin due to incomplete cleaning. This can be prevented by cleaning the resin several time using different solvents, but some impurities may still remain inside the physical structures of the resin, however their effect on the overall PCDD/F concentrations will likely be only minor. (Mroueh U.-M. et al. 1988, p. 16-17)

Sampling and analysis of the samples include a number of possibilities for other errors. The major risks include desorption of PCDD/Fs from particle phase to gas phase, and transformation to other compounds/isomers during the flue gas cooling process. The

risk of transformation increases when sampled at higher temperatures. (Lundin L. 2013) It is also impossible to say how much dioxins are captured or destroyed in the sampling probe and other devices. PCDD/Fs are highly persistent at room temperatures, and therefore no major transformation should occur after the sample is cooled down.

8.2.2 Measurement points

At the CFB boiler plant, PCDD/Fs were measured at five different locations;

- **1 - Before ECO (economizer)**
- **2 - Before ESP (electrostatic precipitator)**
- **3 - Before BHF (bag house filter)**
- **4 - Before Scrubber**
- **5 - Stack.**

The gas phase and particle phase PCDD/Fs were analyzed separately for the locations "Before ECO, Before ESP and Before BHF". Due to the low PCDD/F concentration at the locations after BHF, only the total PCDD/F concentrations were reported.

8.3 Results of the case

The main results of the PCDD/F measurements will be introduced in this chapter. Evolution of the fingerprints between different measurement locations and the gas phase/solid phase partitioning will be reviewed in detail. All the fingerprints are converted to dimensionless values. In the figures, the sum of the 17 congeners represents a 100% emission. The main differences in the absolute concentrations will be discussed in the following chapters.

8.3.1 PCDD/F fingerprints: before ECO, before ESP and before BHF

Examination of the first three measurement points (flue gas downstream) allows us to focus on the evolution of the PCDD/F fingerprints and concentrations through the process. The distribution of the 2,3,7,8-substituted congeners in the particle phase of the 1st measurement day is shown in Figure 8.2. As we see, the amounts of OCDD and OCDF are high compared to the other congeners before the economizer than in other locations. However, the amount of other congeners tends to increase with downstream of the flue gas, which likely results from the temperature drop of about 200 ºC (Table 8.1) between the first and the third measurement point. Due to higher temperature at 'before ECO', more PCDD/Fs seem to be present in the gaseous form. The lower the temperature, the more PCDD/Fs will be adsorbed on fly ash particles. The high concentration of especially OCDD suggests that octachlorinated dioxins are directly formed from aromatic precursors (mainly phenols), and the atmosphere in the eco area is highly favorable for chlorination reactions due to the temperature region.

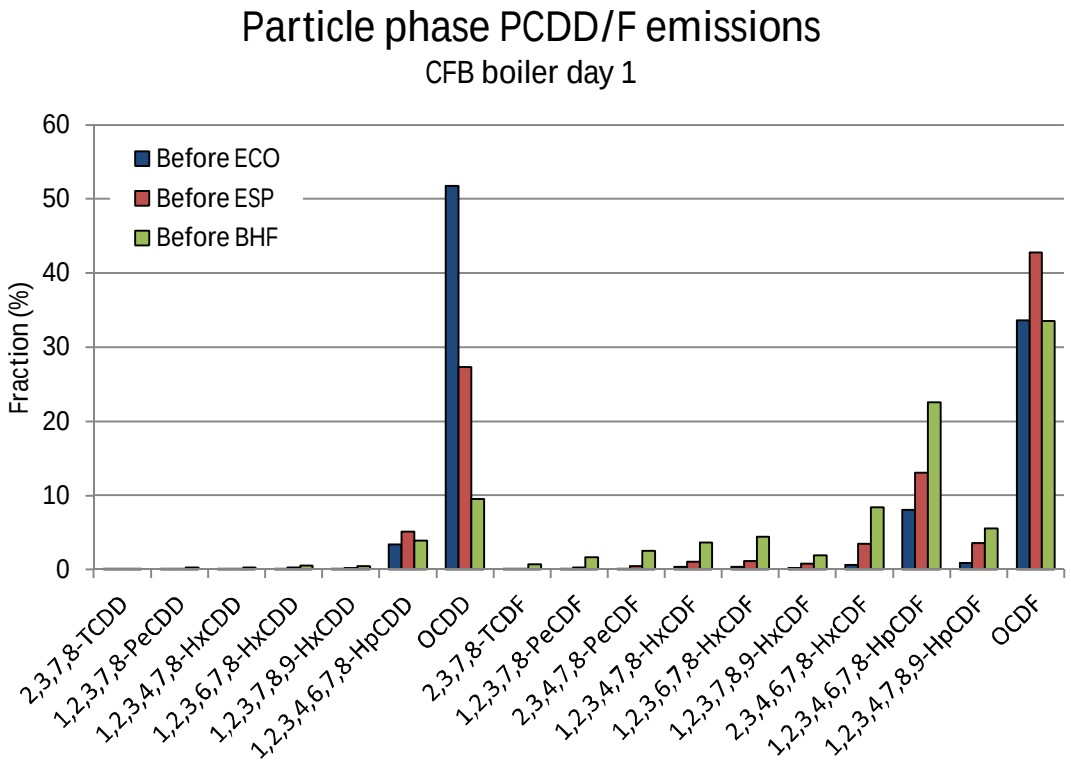


Figure 8.2. *Particle phase PCDD/F fingerprints before the economizer, before the ESP, and before the BHF. Day 1.*

The gas phase PCDD/F fingerprints of the same measurement day are shown in Figure 8.3. The concentrations before the economizer were significantly higher (20-fold) compared to the other two measurement points. In addition, the concentration of gas phase PCDD/Fs was significantly higher than the particle phase PCDD/Fs, especially in the measurement point ‘before ECO’.

Despite the huge variations in the PCDD/F concentrations between the measurement points, the fingerprint remains rather unchanged. This suggests that no remarkable formation occurs in this zone and/or the formation routes remain similar in each measurement locations.

The reason for the high reduction in the gas phase concentrations from ‘before ECO’ to ‘before the ESP’ is a bit unknown, because no flue gas cleaning devices are located between the two locations. We suggests that either it takes place due to the temperature drop of about 200 ºC between this two measurement points causing an intensive decomposition of the PCDD/Fs to other compounds, or the measurement at the higher temperature region is carried out by unsuitable methods. It has be suggested that additional cooling of the sampling probes should be used if sampling above 400 °C (Phan D. et al. 2012), however, the sampling was carried out below this temperature.

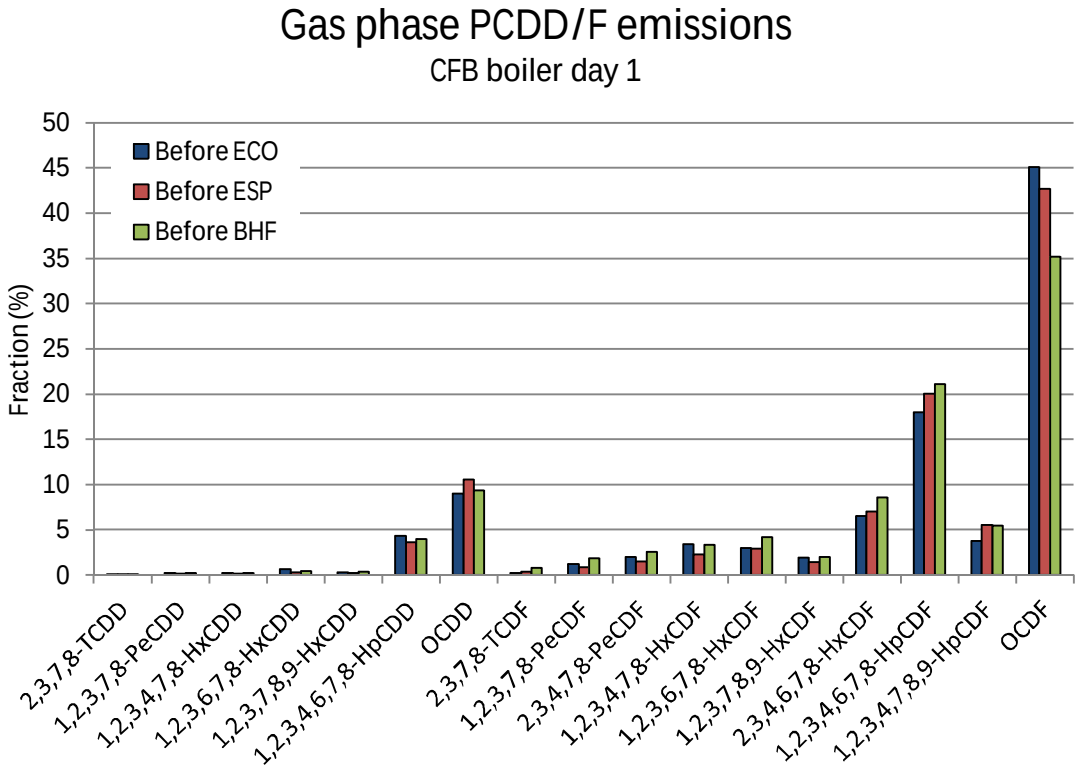


Figure 8.3. *Gas phase PCDD/F fingerprints before the economizer, before the ESP, and before the BHF. Day 1.*

It can also be observed from the Figure 8.3 that the fraction of higher chlorinated congeners increases and the fraction of lower chlorinated congeners decreases between 'before ECO' and 'before ESP. This results from the drop in temperature and different vapor pressures of the congeners; higher chlorinated congeners are easier adsorbed on the fly ash particles, as may be seen from the Figure 8.4 in which the partitioning between the gas phase and solid phase is shown.

On the contrary, the balance between the gas and solid phase PCDD/Fs is changed in the opposite direction in the ESP (Figure 8.3) for most of the congeners. It results from the fact, that the relation between the gas phase and solid phase PCDD/Fs that pass through the ESP is constant, no matter what the vapor pressure of the congener is (Figure 8.5). Therefore, relatively more highly chlorinated congeners (favor the particle phase) are captured by the ESP.

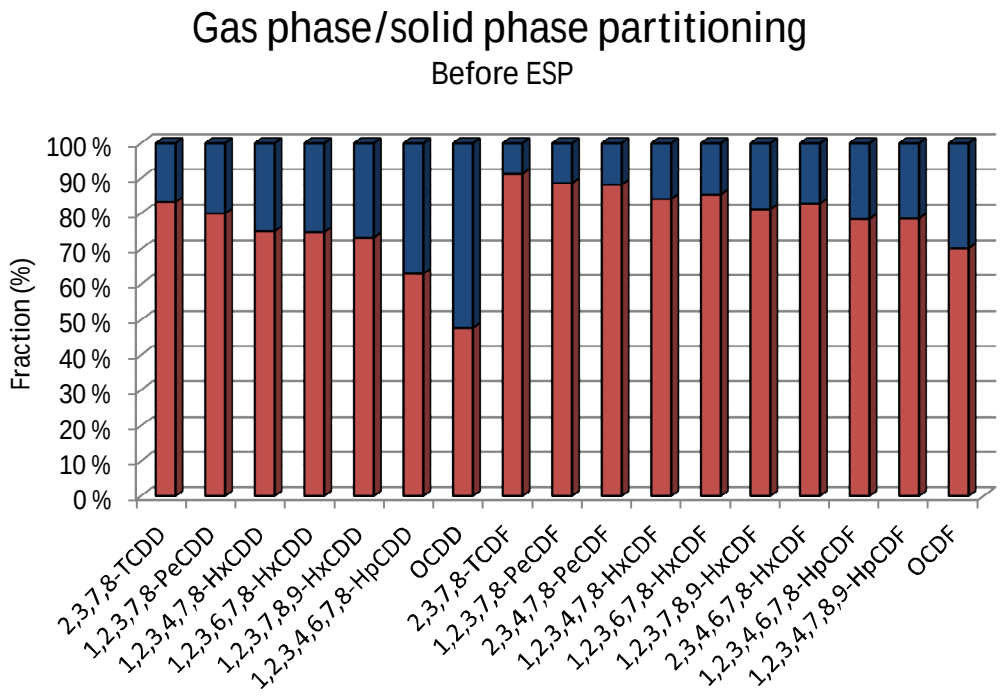


Figure 8.4. *Partitioning between gas phase (red bars) and solid phase (blue bars) PCDD/Fs before the ESP.*

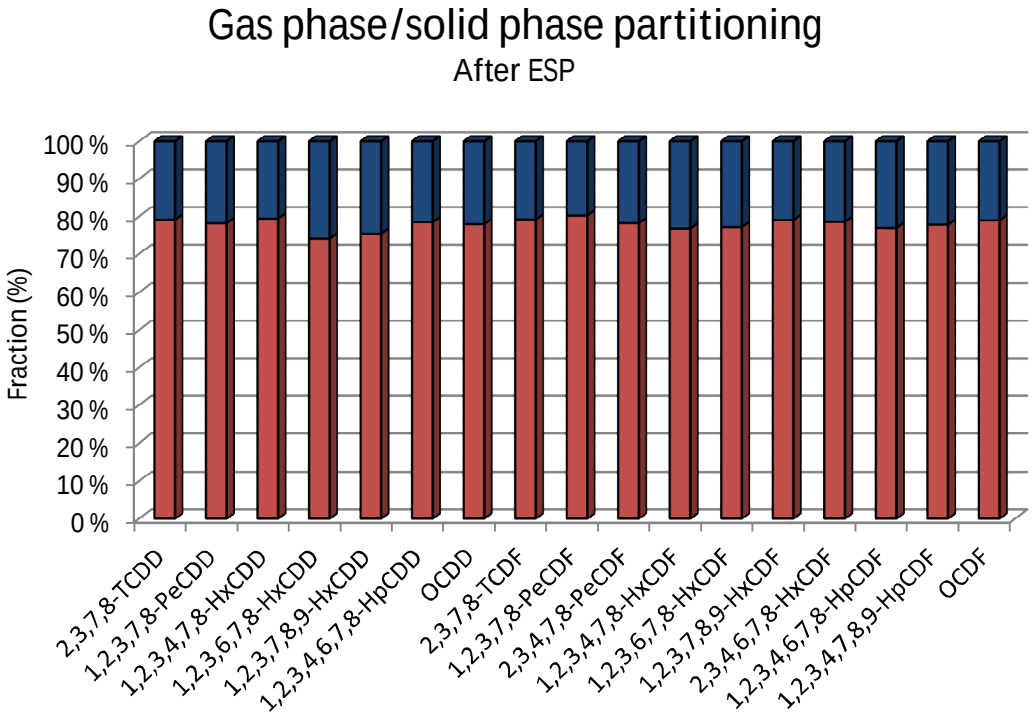


Figure 8.5. *Partitioning between gas phase (red bars) and solid phase (blue bars) PCDD/Fs after the ESP.*

Suchlike fingerprints of the 2nd measurement day are shown in Figure 8.6 and 8.7. The only remarkable difference in the process was the additive sulfur that was fed into the furnace during the 2nd measurement day.

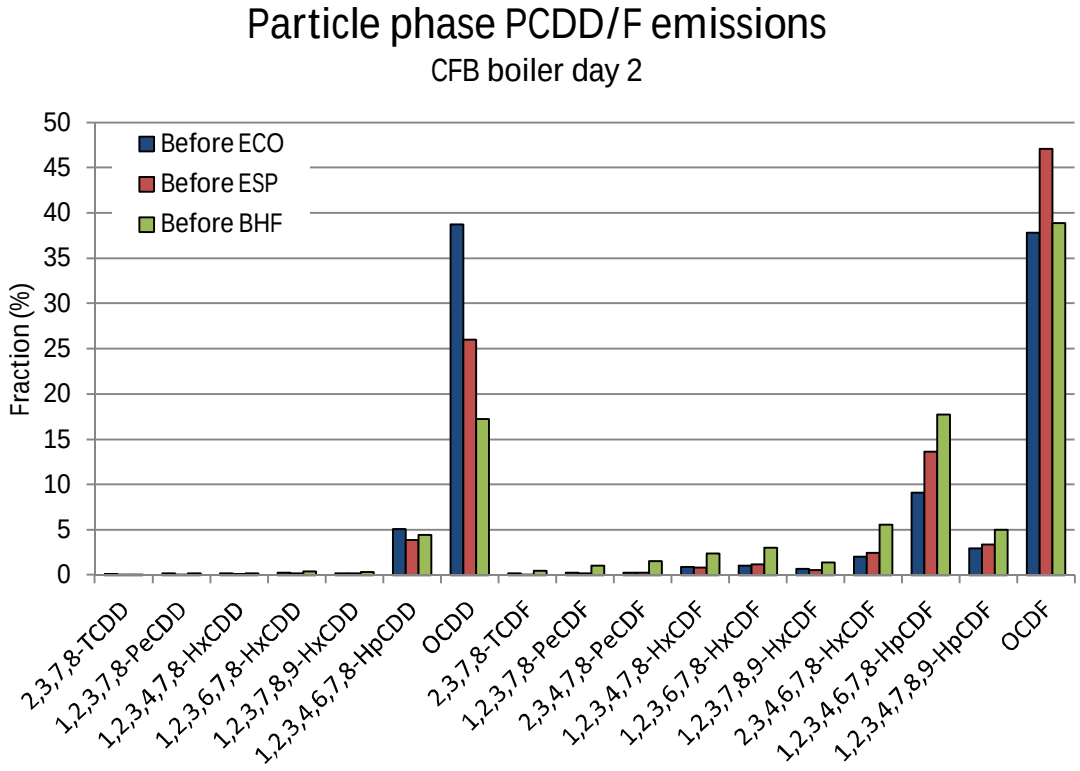


Figure 8.6. *Solid phase PCDD/F fingerprints before the economizer, before the ESP, and before the BHF. Day 2.*

Some significant differences may be found in the fingerprints of the 2nd day compared to those of the 1st day; at first, the amount of OCDF in the gas phase is remarkably lower on the 2nd day (Figure 8.7) compared to the 1st day (Figure 8.3). This may result from the addition of sulfur and its ability to poison the active sites of copper catalysts in the fly ash, thus reducing the chlorination activity of the copper species. Also, the absolute amount of PCDD/Fs in the gas phase was roughly half of the 1st day. However, the role of additive sulfur was supposed to be only minor due to low S/Cl (SO_2/HCl) molar ratio in the flue gases. The higher fuel Cl-%, instead, could be responsible of higher PCDD/F concentrations on day 1. The S/Cl molar ratio was about 0.09 on the 1st day, and about 0.18 on the 2nd day, while a significant reduction is supposed to be achieved at ~0.6 (Raghunathan K. & Gullett B. 1996).

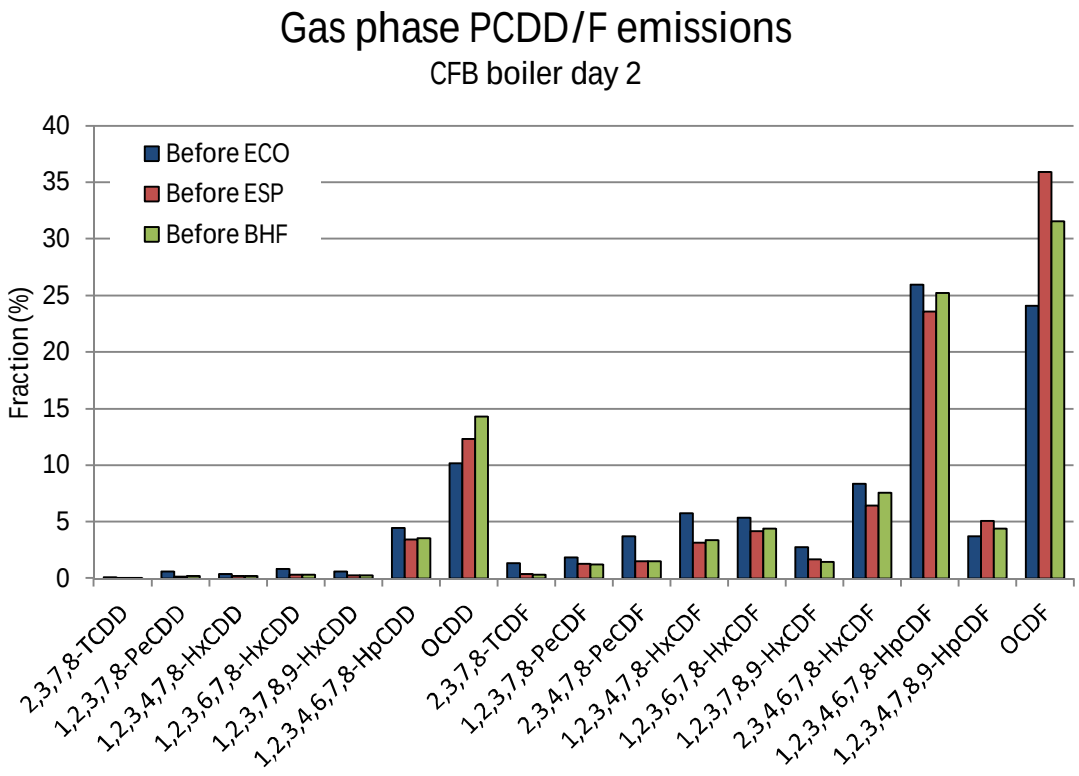


Figure 8.7. *Gas phase PCDD/F fingerprints before the economizer, before the ESP, and before the BHF. Day 2.*

One of the major differences is the intensive increase of gas phase PCDD/Fs on the 2nd day in the ESP; the concentrations measured before the ESP were about one third of the concentrations measured after the ESP (before BHF). This cannot be easily explained by desorption of particle phase PCDD/Fs to the gas phase, because the amount of particle phase PCDD/Fs of the measured congeners 'before ESP' was remarkably lower than the increase of the gas phase PCDD/Fs in the ESP. In addition, large amount of particle phase PCDD/Fs is removed together with the fly ash in the ESP, which removes PCDD/Fs from the process. These findings suggest that either PCDD/Fs are formed in the ESP at temperatures well below 200 ºC probably affected by the high voltage of the ESP, or the sample is not fully representative. The fly ash concentration after the ESP, which seems to correlate with the gas phase PCDD/F concentration after the ESP, was found to be about 3.5 times higher on the 2nd day than on the 1st day during the PCDD/F measurements.

8.3.2 PCDD/F fingerprints: before scrubber and stack

The PCDD/F fingerprints of the two final measurement points are completely different of those before the BHF. This is due to high reduction of PCDD/F in the BHF by feeding of activated carbon. The reduction efficiency is >97% for all samples. The reduction rate is much higher among the furans (>99.6%) due to low reduction efficiency of congeners 1,2,3,4,6,7,8-HpCDD and OCDD (Figure 8.8). These two

congeners, however, account only for about 9% of the toxicity equivalent in the stack due to their low toxicity equivalent factors. The reason of the ability of these two congeners to penetrate the BHF remains unresolved and would need further investigations.

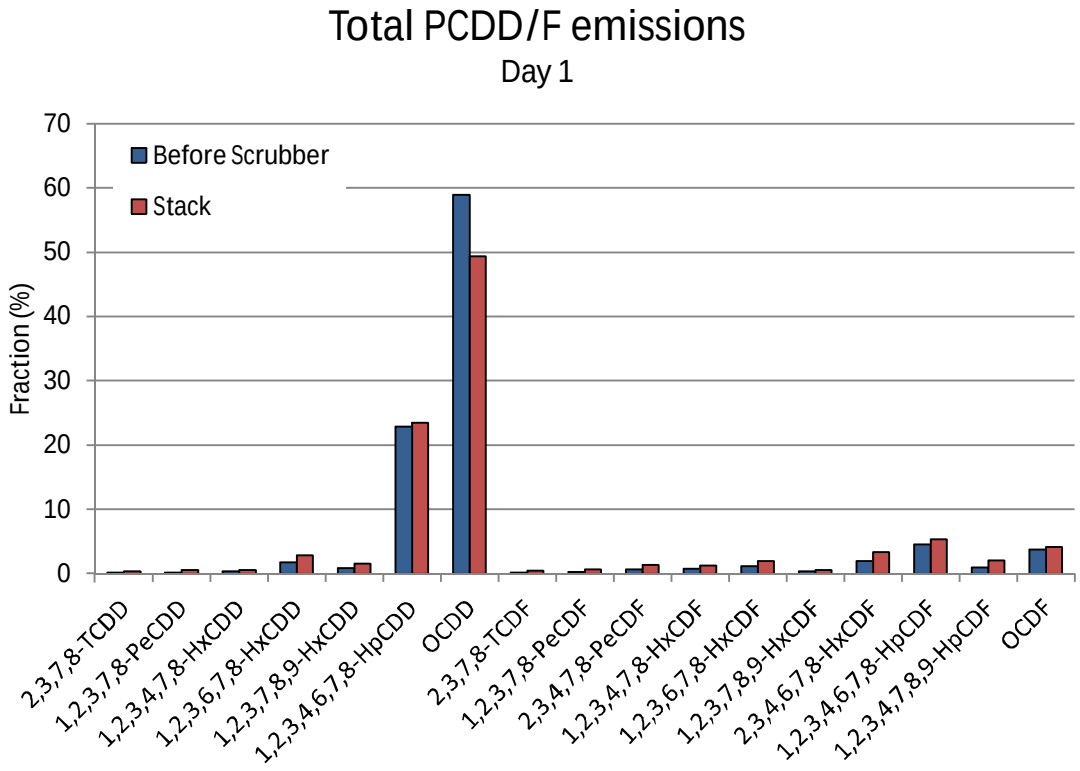


Figure 8.8. *Total PCDD/F fingerprints before the scrubber and in the stack (Day 1).*

The amount of different congeners is evenly reduced in the scrubber and no changes in the fingerprints take place because of the persistent characteristics of PCDD/Fs at lower temperatures.

8.4 Discussion

The fingerprints from the CFB plant is rather similar to those from grate-fired and BFB boilers. The high gas phase PCDD/F fraction in CFB boilers may result from the lower amount of fly ash compared to BFB due to the cyclone separator. The lower fly ash particle size results in high active surface area, which may promote PCDD/F formation through heterogeneous reactions and chlorination of already-formed PCDD/Fs, which could explain the high amount of higher chlorinated congeners. Also, the measurement procedure used in this measurement campaign (cooled probe method) may result in the higher amount of gas phase PCDD/Fs, as the gas phase PCDD/F samples are taken before the filter that captures the particle phase PCDD/Fs. However, the effects of different measurement methods on the results of gas/solid partitioning are not known.

The extremely high gas phase concentration before the economizer followed by intensive reduction in PCDD/F concentration before the ESP remains unclear, although the temperature drop may likely promote the decomposition of the PCDD/Fs. This would mean that an optimal temperature region, where the PCDD/F concentration reaches the maximum, exists. The decomposition PCDD/Fs could be catalyzed by copper compounds in the fly ash.

The congener pattern of the 2nd day suggests that the addition of sulfur could inhibit formation, and especially chlorination reactions of existing PCDD/Fs towards octachlorinated congeners, because the presence of sulfur (SO_2) is found to poison the active sites of copper catalysts by transforming copper chlorides into copper sulfates. The effect of sulfur addition in this case, however, may be minor due to the low S/Cl ratio (~0.2) in the flue gas.

The high fly ash concentration after the ESP seems to increase the gas phase PCDD/F concentrations, thus resulting in higher final PCDD/F concentrations emitted from the stack. The PCDD/F concentrations can increase intensively in the ESP, which may be resulted from the long residence time together with the possible effect of high voltage of the ESP. The behavior of PCDD/Fs in the ESP should be investigated comprehensively in the future.

9 CASE 2: MEASUREMENT CAMPAIGN AT BFB BOILER PLANT

This chapter will concentrate on PCDD/F emission measurement results a bubbling fluidized bed (BFB) boiler plant. The fingerprints will be analyzed and compared to the fingerprints from the CFB boiler presented in Chapter 8.

9.1 Definition of the project

In the spring 2013, a measurement campaign was held at a Metso BFB boiler plant in order to examine the predominant conditions in the furnace and in the flue gas channels. As a part of this measurement campaign, PCDD/Fs and a number of other emissions were measured during two days in order to offer information of the PCDD/F emissions from a BFB boiler and to define the efficiency of flue gas cleaning.

9.1.1 Description of the boiler plant

The main part of the plant is a 65 MW_{th} (80 bar, 470 °C, 24.6 kg/s) BFB boiler that produces electricity and heat for the use of surrounding industrial and municipal area. As fuel, the plant uses demolition wood and wood chips which are transferred by conveyors from an external fuel preparation station situated next to the boiler house. The furnace is followed by an empty pass, 2nd pass (superheaters) and 3rd pass (eco and luvo). Ammonium is injected in the furnace in order to reduce NO_x emissions (SNCR). The flue gas cleaning equipment consists of three parallel bag house filter modules with prior injection of $Ca(OH)_2$ and activated carbon.

9.1.2 Fuel and additives during the measurements

The demolition wood (DW) fuel is transported to the site mainly from Sweden and United Kingdom (UK). Therefore, changes in the quality of the fuel are possible. The fuel of the 1st day consisted only of British DW, while a mixture of Swedish and British DW was used on the 2nd day. An example of the fuel sample used can be seen in Figure 9.1. Since no MSW is combusted, the chlorine and copper contents of the fuel are lower than in the fuel used at the CFB boiler of the Case 1. The measured Cl-content of the fuel samples of days 6th and 7th March were 0.36 and 0.35, respectively. The fuel moisture was 21.8% on the 1st day) and 28.9% on the 2nd day.

The daily averages of the ammonium injection were even on both days (86 l/h). The ammonium slip was little bit higher on the 2nd day, as 34 mg/m^{3}n (1st day) and 64

mg/m^{3}n (2nd day) were measured before the bag house filter. $Ca(OH)_2$ was injected at rate of 40 kg/h and activated carbon at 50 mg/m^{3}n.

Figure 9.1. *Demolition wood fuel sample. (Merja Hedman).*

9.1.3 Boiler operation and temperatures during the measurement

The operation of the boiler was generally rather stable during the PCDD/F measurements. Almost daily, the boiler operation is disturbed by blocking of the rotary fuel feeders. This can be followed by an intensive drop of up to 100 °C (see Figure 9.2) in the furnace temperatures. The blockages are solved in a short period of time, but the time required to normalize the boiler operation may take about half an hour. A short blockage took place on the 1st measurement day, but no major fluctuation in the temperatures could be observed hence no remarkable effects on PCDD/F emissions are expected.

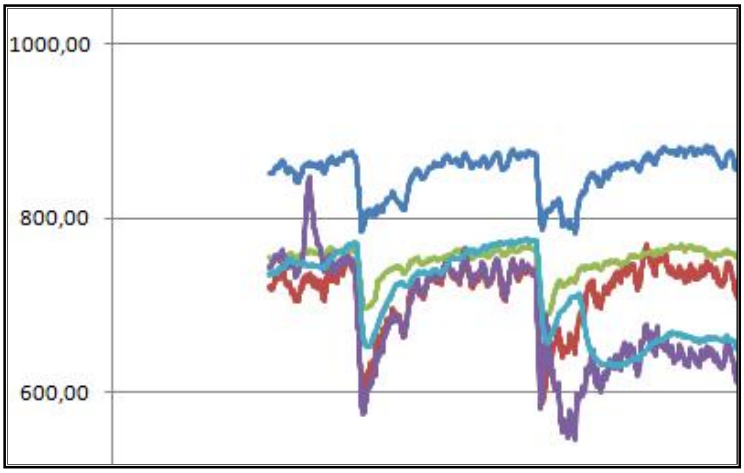


Figure 9.2. *The effect of rotary feeder blockages on furnace temperatures (°C).*

Boiler trips are found to remarkably increase PCDD/F emissions in grate-fired waste incinerators. However, fluidized bed boilers are less vulnerable for varying operating conditions when it comes to the production of PCDD/Fs or other emissions (DeFusco et al. J. 2007).

9.2 Measurement procedure

The execution of the PCDD/F measurements and the measurement points will be shortly described in this chapter.

9.2.1 Measurement standard and procedure

The measurements were completed according to the PCDD/F measurement standard EN-1948-1. In this measurement, the filter/condenser method (Figure 9.3) was used The PCDD/F measurement equipment used in the measurements may be seen from the Figure 9.4.

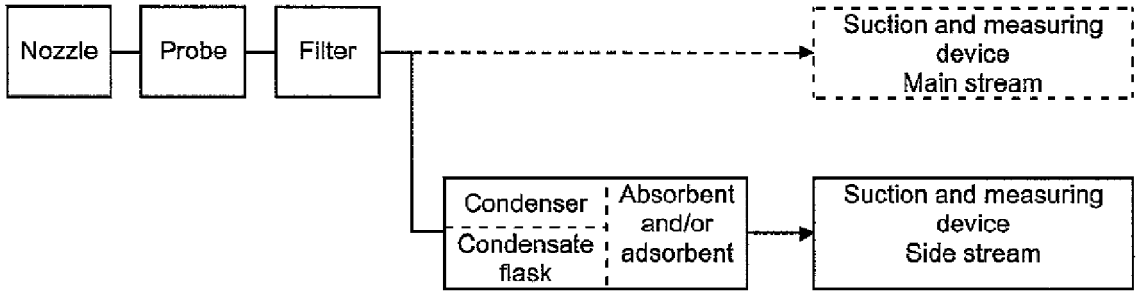


Figure 9.3. *Schematic representation of the filter/condenser method. (S/EN1948-1/2006, p. 13)*

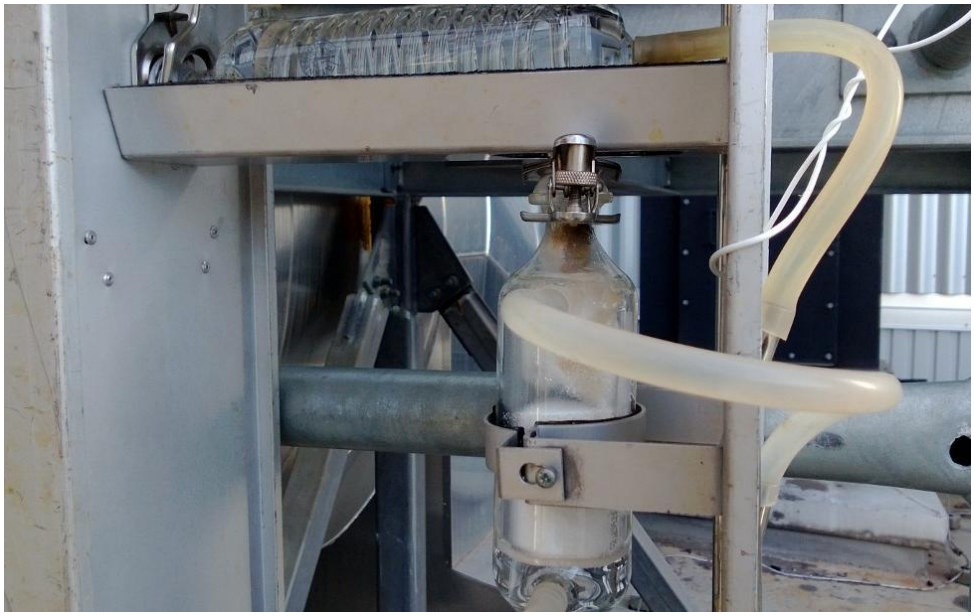


Figure 9.4. *Part of the PCDD/F measurement equipment; quartz filter, water cooler and XAD-2 cartridge. (Juha Jokiluoma).*

In the filter/condenser method, the flue gas sample travels through a glass fiber filter usually placed after the probe on which the fly ash particles including the solid phase PCDD/Fs are captured. The filter is kept below 125 ºC to avoid chemical reactions during the sampling, however keeping it above the flue gas dew point. The gas phase travels through the filter and is cooled below 20 ºC in a water cooler. This is followed by a XAD-2 resin which adsorbs the gas phase PCDD/Fs. Some PCDD/Fs are adsorbed on the surfaces of the water cooler. All the gas-carrying parts are rinsed and with acetone and toluene resulting in three different PCDD/F samples; quartz filter, XAD-2 resin, and PCDD/F condensed on surfaces of the water cooler. (S/EN1948-1/2006)

Three separate PCDD/F samples, which may be later combined, are obtained in this method; filter sample, XAD-2 resin sample, and water cooler condensate sample. In this experiment, the particle phase sample consists of the quartz filter and water cooler condensate, and the gas phase sample involves only the XAD-2 sample. That is to say, a small amount of the PCDD/F passing through the quartz filter (and condensed on the walls of water cooler) is also included in the solid phase PCDD/Fs.

In the water cooler method used in Case 1, the gas phase PCDD/F sample consists also only of the XAD-2 resin sample, however, the measurement equipment assembly is different, which may cause differences on the gas/solid partitioning of the PCDD/Fs.

9.2.2 Measurement points

The PCDD/Fs were measured during two days at two different locations. The first measurement location was inside a horizontal flue gas duct before the bag house filters. The second measurement point was located in a horizontal duct just after the bag house filters and the I.D. fan (induced draft fan).

9.3 Results of the case

In this chapter, the main results of the PCDD/F emissions measurements will be reviewed and the PCDD/F fingerprints will be analyzed and compared with the results from the measurement campaign at the CFB boiler (Chapter 8).

9.3.1 PCDD/F fingerprints before BHF

The fingerprints from this particular BFB plant differ a lot from those of grate-fired MSWIs and CFB boiler presented in the previous chapter. The congener distribution of the 2,3,7,8-substituded PCDD/F congeners measured before the bag house filters can be seen in Figure 9.5 (1st day) and 9.6 (2nd day). The total amount of PCDD/Fs on 2nd day was about three times greater than on the 1st day. The solid phase PCDD/Fs clearly dominated on both measurement days, unlike at the case CFB boiler.

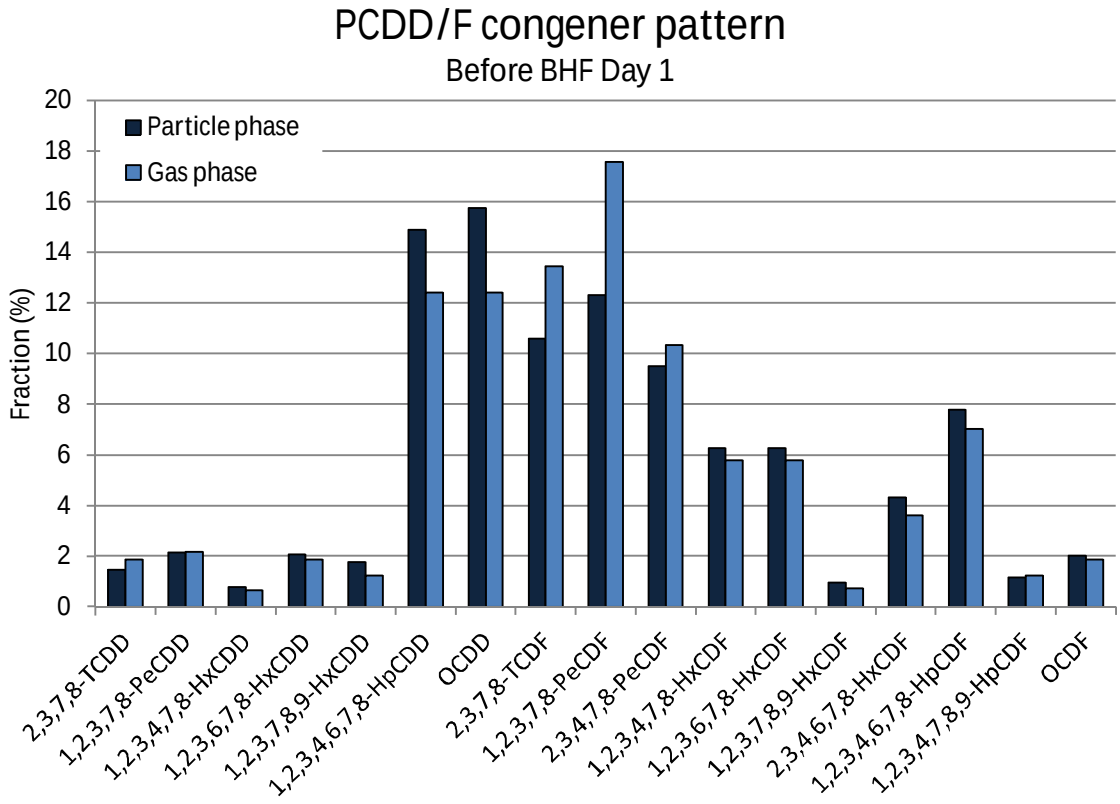


Figure 9.5. *PCDD/F fingerprints before the bag house filter. (Day 1).*

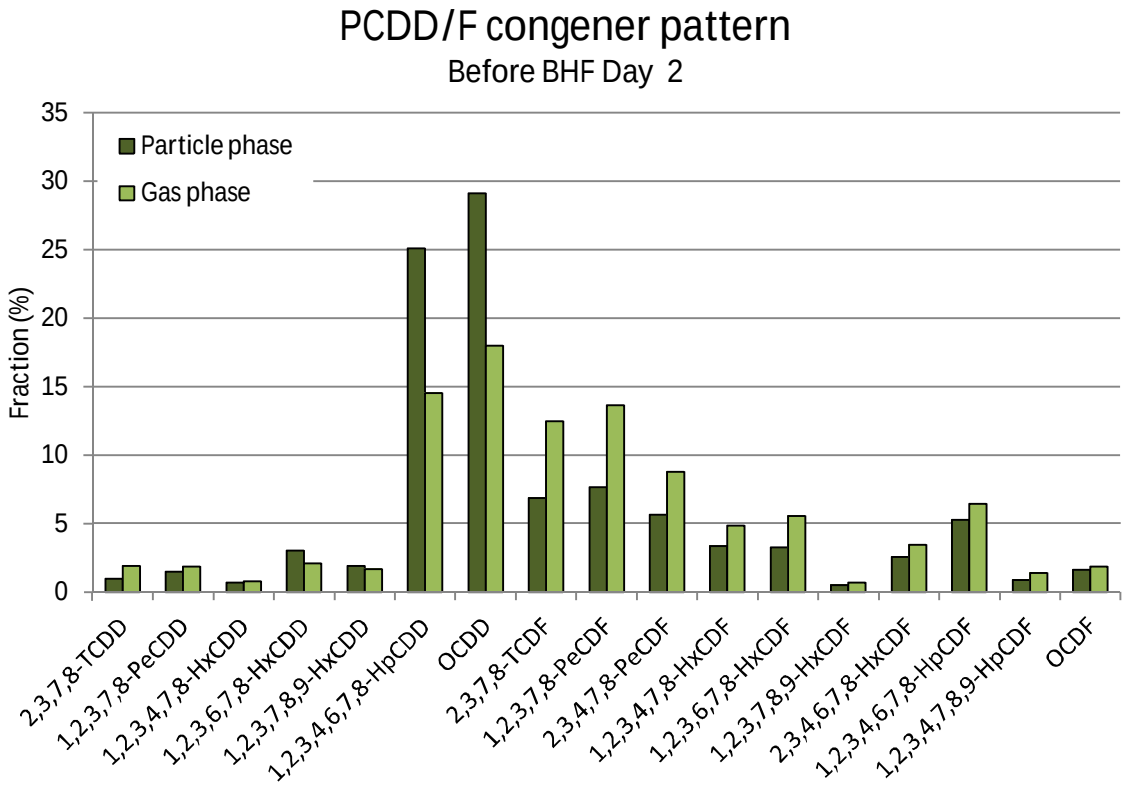


Figure 9.6. *PCDD/F fingerprints before the bag house filter (Day 2).*

If we consider the group of PCDDs, we realize that it reminds a lot those from other power plants presented in Chapters 7 and 8; tetra- to hexachlorinated dibenzo-*p*-dioxins are present only in minor amounts and 1,2,3,4,6,7,8-HpCDD and OCDD dominate over the other PCDD congeners. This indicates that PCDDs are formed through similar pathways in all those processes; most likely via condensation of phenol precursors (precursor mechanism). The proportions of 1,2,3,4,6,7,8-HpCDD and OCDD were little bit higher in gas phase sample on the 2nd day (Figure 9.6) suggesting that more precursors or more catalyst may have been present, which possibly results from differences in fuel characteristics. The formation of these congeners seems to be highly favored among the PCDDs. The fuel Cl-concentrations measured were 0.36 (6th March) and (0.35), and the copper level was higher on the 6th day, which are completely opposite results as expected. However, individual fuel samples do not offer complete information of the copper or chlorine concentrations of the whole measurement period.

The group of furans, however, looks completely different than in the previous examples and results. Tetra- and pentachlorinated furans are present in larger amounts, while the higher chlorinated congeners only exist in minor amounts. This is clear evidence that different formation pathways dominate in this BFB boiler and in the CFB boiler of Chapter 8.

Despite the large amount of fly ash (compared to grate-fired boilers), the exiguity of higher chlorinated furans, especially 1,2,3,4,6,7,8-HpCDF and OCDF indicates that the role of de novo synthesis and fly ash-catalyzed chlorination reactions play an insignificant role in this BFB boiler plant. Most likely this results from lower amount of catalyzing and chlorinating components in the fly ash and in the flue gases, in other words, from the low amount of copper chlorides and HCl. The condensation of phenols may also be responsible of the formation of furans, as suggested by Ryu J.-Y. et al. (2006). They also suggested that the role of metal-catalyzed phenol condensation in formation of especially lower chlorinated furans could be significant. The formation of furans in this case will most likely follow the route; formation of unchlorinated DF from phenols, which is followed by further chlorination of the DFs to form PCDFs. Additionally, direct formation of PCDFs from chlorinated phenols is also possible.

If we take a look to the PCDD/F congener pattern weighted by the toxic equivalent factors, we may see (Figure 9.7) that substantially the largest fraction of the toxic equivalent belongs the 2,3,4,7,8-PeCDF and tetrachlorinated congeners, the reduction of which is necessary in order to meet with the emissions limits of this plant (0.1 ng/m^{3}n, 11%-O_2, dry gas). This can be clearly achieved by the flue gas cleaning equipment designed for this plant (bag house filters with prior injection of $Ca(OH)_2$ and activated carbon.

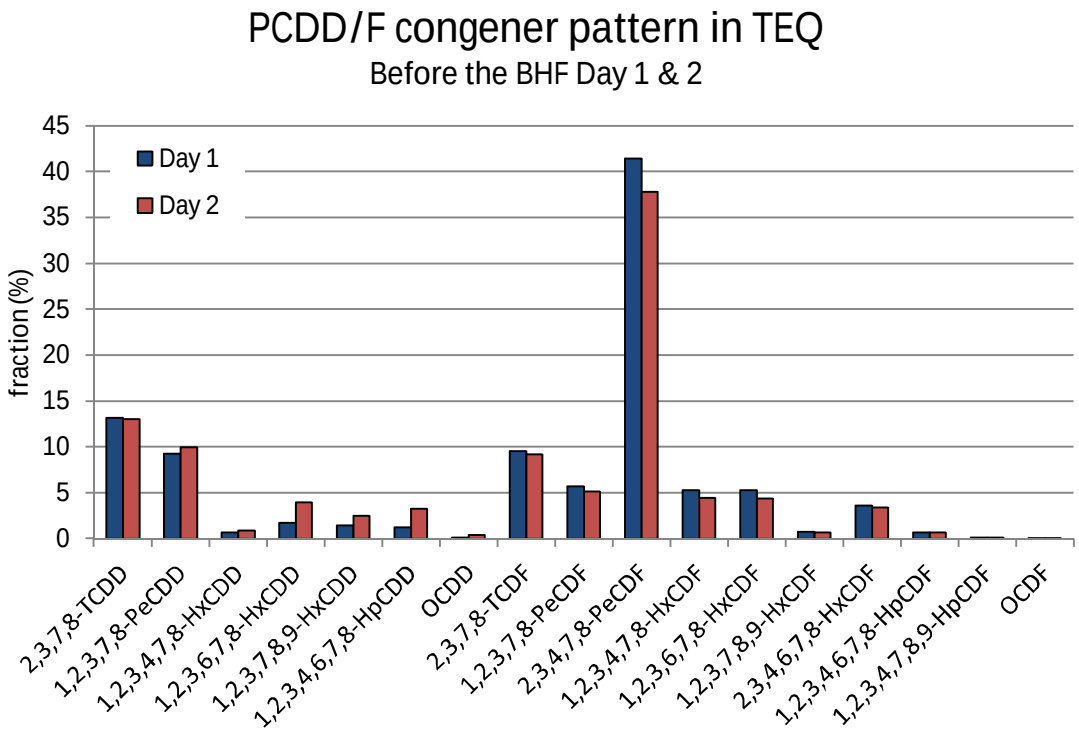


Figure 9.7. *PCDD/F fingerprints (gas + solid phase) weighted by the toxicity equivalent factors before the BHF.*

9.3.2 PCDD/F fingerprints after BHF

The PCDD/F concentrations measured after the bag house filter were extremely low and the concentration of most of the congeners was below the detection limit. Only few congeners (1,2,3,4,6,7,8- PCDD and OCDD, 2,3,7,8-TeCDF and 1,2,3,4,6,7,8-HpCDF) were detectable, though the concentrations were about 100 times lower than before the BHF. As a point of comparison, the field blanks from the samples before the BHF were of the same magnitude, or even higher. This proves that the bag house filters with prior injection of $Ca(OH)_2$ and activated carbon is a extremely suitable method for minimizing PCDD/F and other emissions, especially when operated at lower temperatures (~150 ºC).

9.4 Discussion

The PCDD/F fingerprints from the case BFB plant are substantially different of those from the case CFB boiler (Chapter 8) and from grate-fired MSW incinerators presented in the literature.

The amount of fly ash, which is found to correlate with PCDD/F emissions, is higher in BFB boilers than in CFB or grate-fired boilers. Therefore, it could be expected that fly ash-catalyzed formation from residual carbon (de novo synthesis) would be the governing formation pathway in this particular plant. However, since no SRF or MSW are combusted in this plant, the amount of copper (chlorides) found in the fly ashes is

lower when only demolition wood is combusted. The presence of copper chlorides promotes intensive formation furans and chlorination of unchlorinated DD/Fs and PCDD/Fs towards higher chlorinated congeners. These reactions are supposed to play a minor role in this particular plant and the formation of PCDD/F is supposed to be governed mainly by condensation of phenol precursors. This is likely the main reason for the differences in the fingerprints between this BFB boiler and the CFB boiler presented in the Chapter 8.

In the Figure 9.8 below, PCDD/F fingerprints from the Case 1 CFB boiler (red bars) and from another CFB boiler combusting municipal and industrial waste (blue bars) are shown. The blue fingerprint seems to be almost completely similar to the fingerprint of the case CFB boiler presented in Chapter 8. In both plants, the chlorine content of the fuel is rather high.

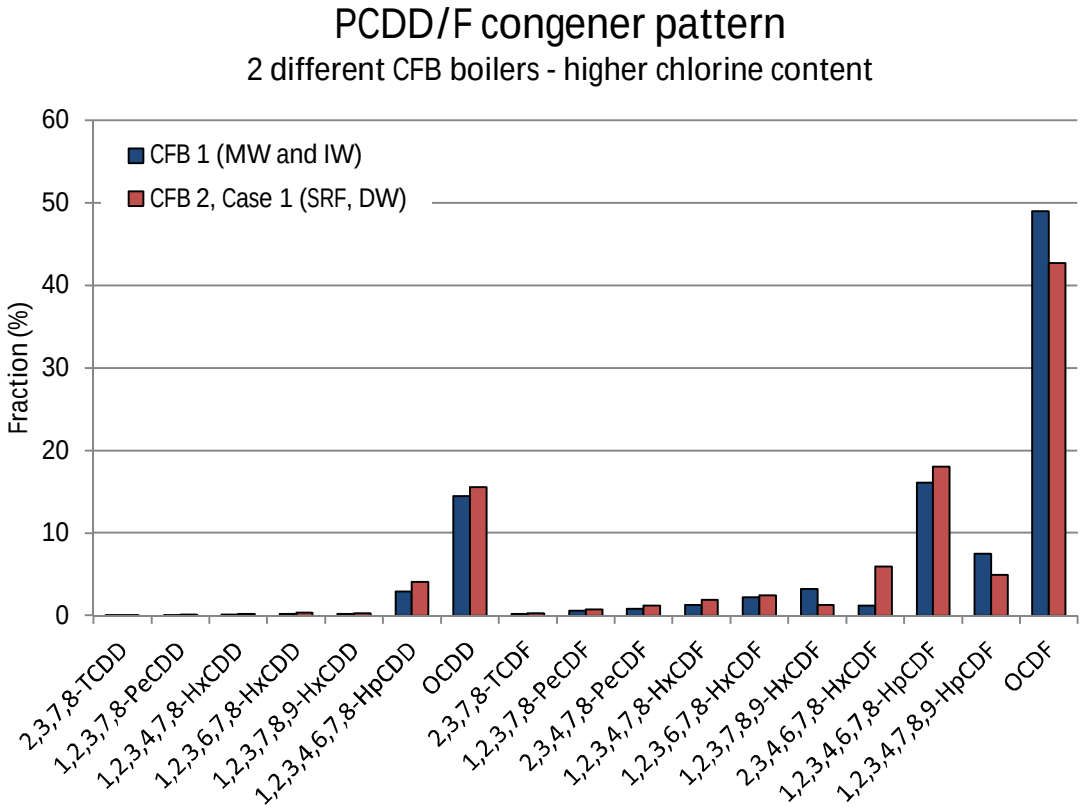


Figure 9.9 *PCDD/F fingerprints from two CFB boiler combustion fuel of higher chlorine content (~0.5-2%).*

In the figure 9.9, fingerprints from the case BFB boiler and CFB boiler combusting coal, peat biomass and SRF are shown. These fingerprints differ from those shown in Figure 9.8 above. Also, the fingerprint from the aluminum sintering plant (see Figure 7.2) is rather similar with these fingerprints. The fuels used in these plants contain less chlorine than in the two CFB boilers presented above (Figure 9.8). These findings suggest that the main affecting factors that define the PCDD/F fingerprints are most

likely related to the composition and quality of the fuel rather than to the combustion technology itself.

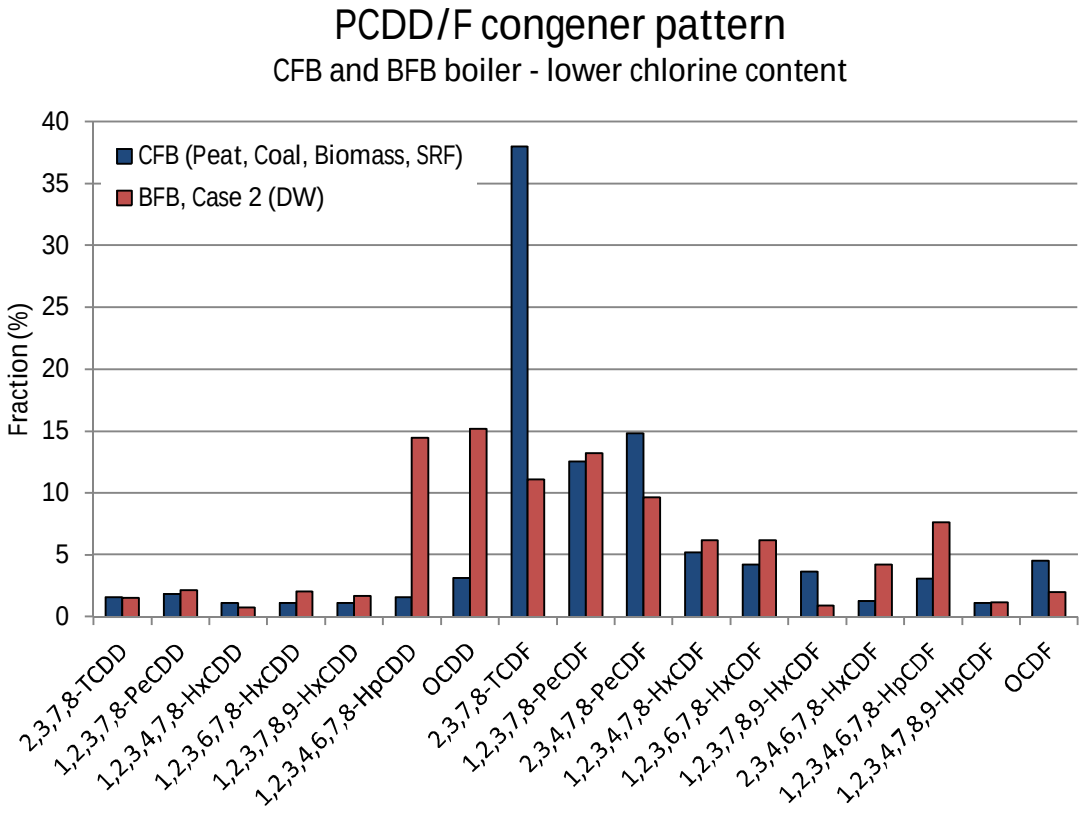


Figure 9.8. *PCDD/F fingerprints from a BFB and a CFB boiler combusting fuel of lower chlorine content (<1%).*

10 UNCERTAINTY OF THE MEASUREMENT RESULTS

There are a number of factors that increase the level of uncertainty of the PCDD/F measurements. The overall uncertainty of the PCDD/F measurement and sampling, which is announced in the measurement reports, is commonly about 30%.

A significant uncertainty is related to the proper cleaning of the sampling equipment. Since the PCDD/F concentrations measured are minimal, even a small amount of impurities may result in relatively high deviations in the results. Therefore, control blanks must to be taken. The values of control blanks at the case 1 CFB boiler were taken only before the 2nd measurement day. The concentrations of all congeners were below the detection limit. At the case 2 BFB boiler plant, 0.0008 (lower bound) and 0.012 (upper bound) ng/m^{3}n I-TEQ were measured before the BHF and all values were below the detection limit after the BHF.

In the first case (Chapter 8), sampling at the temperatures of about 350 °C makes us suspicious of the reliability of the results; significantly higher values were measured at the eco area compared to other measurement points. However, sampling at these temperatures should be possible and even higher PCDD/F concentrations are not uncommon in waste incineration processes.

Usually, statutory sampling of PCDD/Fs is carried out for a period of 6 hours to ensure that the PCDD/Fs levels are above the detection limits. In the CFB case, the results are average values of measurement periods of three hours, which must be considered. In the BFB case, the PCDD/Fs were measured during a period of 6 hours.

The gas phase/solid phase partitioning may highly depend on the measurement procedure and fly ash composition, which may cause high variation in the results. For instance, PCDD/Fs attached on the quartz glass filter might be released to the gas phase and pass the filter, which may increase the fraction of gas phase PCDD/Fs. Therefore, it would be better to consider PCDD/Fs as one total sample.

Significant uncertainty is related to the fuel quality that is difficult to measure. The fuel samples are taken randomly from an unhomogenous fuel mixture. A clear correlation between PCDD/F emissions and the fuel in conventional power plants is difficult to develop. In addition, the boiler operation may highly affect the formation of PCDD/Fs. Since the formation of PCDD/Fs seems to be a highly complex process depending on many factors, the final PCDD/F emission and shape of the fingerprint is highly challenging to predict.

11 CONCLUSION

The aim of this thesis work was to define the major differences in the formation of poly-chlorinated dibenzo-*p*-dioxins/dibenzofurans in combustion of solid waste. In conclusion, the overall formation of PCDD/Fs seems to be a highly complex process. However, the main formation routes are supposed to involve three major routes, which are taking place both in grate-fired and fluidized bed combustion of waste; homogeneous formation from aromatic precursors in the gas phase at high temperatures, heterogeneous formation from aromatic precursors on surfaces of copper catalysts, and heterogeneous formation from residual carbon in the fly ash in presence of copper catalysts. The formation mainly takes place in the post-combustion zones at temperatures from about 200 to 500 °C through the heterogeneous formation pathways. In fluidized bed combustion, the combustion of the fuel is more complete compared to grate-fired boilers, which decreases PCDD/F emissions due to lower amount of aromatic precursors and residual carbon that result from incomplete combustion of the fuel. However, the amount of fly ash is significantly higher in fluidized bed boilers than in grate-fired boilers, which increases the possibility of PCDD/F formation in the post-combustion zone.

In the PCDD/F emission measurements carried out at two fluidized bed boiler plants, only information of the 17 toxic 2,3,7,8-substituted PCDD/Fs was obtained. In order to define the governing formation routes, the amounts of all 210 PCDD/F congeners should be analyzed. These data should be compared with the fingerprints from known reactions and from known precursor compounds, which however would extremely onerous. Generally, the fingerprints from all waste combustion processes vary only little. This results from similar fuel characteristics and process parameters of same magnitude. In the CFB boiler plant, the fuel contained more copper and chlorine, which increases PCDD/F formation via heterogeneous pathways, and chlorination of the already-formed PCDD/Fs towards higher chlorinated congeners. This is likely one major factor that affects on the shape of PCDD/F fingerprints at the two case boiler plants. Due to large variations in the fuel characteristics in these boiler plants, the definition of the effect of the combustion technology itself is challenging. The differences that are found in the literature between fluidized bed boilers and grate-fired boilers are suggested to occur due to differences in the fly ash characteristics, which results from the feeding of NH_3 or urea in the furnace in fluidized bed boilers. Other additives, such as $CaCO_3$ or CaO, may also affect the formation of PCDD/F fingerprint by participating in the PCDD/F formation reactions or by transferring the pH of the fly

ash towards more alkaline side. However, no definite conclusions of their effect on PCDD/F fingerprints can be made, if information of only 17 congeners is available.

Several species, especially sulfur, are found to inhibit PCDD/F formation. The inhibitive effect of sulfur is supposed to originate from its ability to transfer copper chlorides in the fly ash to copper sulfates. Copper sulfates are less active catalysts than copper chlorides. The PCDD/F fingerprints in the CFB boiler were found to be affected by the feeding of sulfur; the fraction of the higher chlorinated congeners was reduced. This finding coincides with previous investigations, thus the chlorination was supposed be more limited with more SO_2 in the flue gases. In this case, however, the effect of sulfur remains somewhat unclear due to low S/Cl ratio in the flue gases.

PCDD/Fs can be effectively removed by a bag house filter with prior injection of activated carbon if operated at temperatures below 200 °C in order to avoid formation of PCDD/Fs in the dust cakes on the filter fabrics. At higher temperatures, more PCDD/Fs may transfer to the gas phase from the particle surfaces and penetrate the filter fabrics. Hepta- and octachlorinated PCDDs were found to be able to penetrate through the filter fabrics, while the other congeners were captured effectively. The reason for this, however, remains unresolved. Electrostatic precipitators may act as possible sources of PCDD/Fs if operated above 200 °C and even at lower temperatures. Especially the gas phase PCDD/Fs were found to significantly increase in the ESP, which could not be explained by desorption of PCDD/Fs from the particle phase to the gas phase, because the amount of PCDD/F in the solid phase was clearly lower before the ESP than the increase of the gas phase PCDD/Fs in the ESP. However, since the overall amounts of PCDD/Fs are not known, no definite conclusions can be made. The effect of the high voltage field on PCDD/F formation remains unclear, but it is suggested that it could promote PCDD/F formation. This topic should be investigated in the future. A comprehensive analysis of the total PCDD/F mass balance over the ESP, including the ash samples, could be a suitable method for that.

The gas/solid phase partitioning was analyzed. The gas phase PCDD/Fs were found to dominate in the CFB plant, while the solid phase PCDD/Fs were found to dominate in the BFB plant. This can result from the differences in the fly ash composition; the mean particle size of the fly ash is smaller in CFB boiler, which may influence the gas/solid balance. The role of the fly ash composition in the PCDD/F partitioning, however, is unclear. Another affecting factor is the temperature. At higher temperatures, more PCDD/Fs are present in the gas phase. In addition, the gas/solid partitioning of different congeners differ due to different vapor pressures of the congeners. The temperature, however, cannot fully explain the huge differences in the gas/solid partitioning between the two boiler plants, because the temperatures at the locations before the bag house filter, for instance, varied only about 20 °C between these two boilers. Third reason for the differences in the gas/solid partitioning may be the differences in the measurement procedures used at the two plants. The effect of different methods and measurement temperatures on gas/solid partitioning should be investigated.

REFERENCE

A. J. Chandler & Ltd. 2006. Review of Dioxins and Furans from Incineration In Support of a Canada-wide Standard Review. A report prepared for The Dioxins and Furans Incineration Review Group through a contract associated with CCME Project # 390-2007. 216 p.

Abad, E., Caixach, J. & Rivera, J. 1997. PCDD/PCDF from Emission Sources and Ambient Air in Northeast Spain. Chemosphere, 35, no. 3, pp. 453-463.

Abad, E., Adrados, M., Caixach J. & Rivera J. 2002. Dioxin Abatement Strategies and Mass Balance at a Municipal Waste Management Plant. Environmental Science & Technology, 36, pp. 92-99.

About.com. Briefing: The Seveso Disaster. 2012. [WWW]. [Cited: 18.12.2012]. Available at: http://ec.europa.eu/environment/seveso/index.htm

Addink, R., Bakker, W. & Olie, K. 1995. Influence of HCl and Cl_2 on the Formation of Polychlorinated Dibenzo-p-dioxins/Dibenzofurans in a Carbon/Fly Ash Mixture. Environmental Science & Technology, 29. pp. 2055-2058.

Addink, R. & Olie, K. 1995. Mechanisms of Formation and Destruction of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Heterogeneous Systems. Environmental Science & Technology, 29, pp. 1425-1436.

Addink, R., Cnubben, P. & Olie, K. 1995. Formation of Polychlorinated Dibenzo-p-dioxins/Dibenzofurans on Fly Ash from Precursors and Carbon Model Compounds. Carbon, 33, pp. 1463-1471.

Addink, R., Antonioli, M., Olie, K. & Govers, H. 1996a. Reactions of Dibenzofurans and 1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin on Municipal Waste Incinerator Fly Ash. Environmental Science & Technology, 30, pp. 833-836.

Addink, R., Paulus, R. & Olie, K. 1996b. Prevention of Polychlorinated Dibenzo-p-dioxins/Dibenzofurans Formation on Municipal Waste Incinerator Fly Ash Using Nitrogen and Sulfur Compounds. Environmental Science & Technology, 30, pp. 2350-2354.

Altarawneh, M., Dlugogorski, B., Kennedy, E. & Mackie, J. 2009. Mechanisms for Formation, Chlorination, Dechlorination and Destruction of Polychlorinated Dibenzo-p-

dioxins and Dibenzofurans (PCDD/Fs). Progress in Energy and Combustion Science. 35, p. 245-274.

Aurell, J. & Marklund, S. 2009. Effects of Varying Combustion Conditions on PCDD/F Emissions and Formation During MSW Incineration. Chemosphere, 75, pp. 667-673.

Babushok, V. & Tsang, W. 2001. Gas-phase Mechanism for Dioxin Formation. Chemosphere, 51, pp. 1023-1029.

Bajamundi, C. 2011. Insights in the Formation of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans. VTT Technical Research Centre of Finland. Internal Report. p. 89.

Bajamundi, C. 2013. VTT Technical Research Center of Finland. Internal Progress Report. p. 14.

Bonte J., Fritsky K., Plinke M., Wilken M. 2001. Remedia Catalytic Filter System. Catalytic Destruction of PCDD/F in a Fabric Filter. Technical paper. Presented at the 2001 International Conference on Incineration and Thermal Treatment Technologies, Philadelphia, Pennsylvania, USA. [PDF]. [Cited: 20.2.2013] Available at: http://www.gore.com/MungoBlobs/901/674/remedia_case_inc_belgium.pdf

Born, J., Louw, R. & Mulder, P. 1989. Formation of Dibenzodioxins and Dibenzofurans in Homogenous Gas-Phase Reactions of Phenols. Chemosphere, 19, pp. 401-406.

DeFusco, J., McKenzie, P. & Fick M. Bubbling Fluidized Bed or Stoker – Which is the Right Choice for Your Renewable Energy Project?, Presented in: CIBO Fluidized Bed Combustion Conference, May 21-23, 2007, Lexington, Kentucky, USA. Babcock & Wilcox Company. p. 6.

Dickson, L., Lenoir, D. & Hutzinger, O. 1992. Quantitative Comparison of De Novo and Precursor Formation of Polychlorinated Dibenzo-p-dioxins under Simulated Municipal Solid Waste Incinerator Postcombustion Conditions. Environmental Science & Technology, 26, pp. 1822-1828.

European Commission. 2012. Chemical Accidents (Seveso III) – Prevention, Preparedness and Response. [WWW]. [Cited: 18.12.2012]. Available at: http://ec.europa.eu/environment/seveso/index.htm

Everaert, K. & Baeyens, J. 2002. The Formation and Emission of Dioxins in Large Scale Thermal Processes. Chemosphere, 46, pp. 439-448.

Fiedler, H. 2003. The Handbook of Environmental Chemistry, 3, part O. Persistent Organic Pollutants, Springer-Verlag, Berlin Heidelberg. pp. 123-173.

Fujimori, T., Takaoka, M., Kato, K., Oshita, K. & Takeda, N. 2007. Understanding Atacamite as a Copper Catalyst for De Novo Synthesis by Heating Experiment and Dispersive XAFS. Organohalogen Compounds, 69, pp. 319-322.

Fängmark, I., Strömberg, B., Berge, N. & Rappe, C. 1994. Influence of Post-combustion Temperature Profiles on the Formation of PCDDs, PCDFs, PCBzs and PCBs in a Pilot Incinerator. Environmental Science & Technology, 28, pp. 624-629.

Gullett, B., Bruce, K. & Beach, L. 1990. The Effect of Metal Catalysts on the Formation of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofuran Precursors. Chemosphere, 20, pp. 1945-1952.

Gullett, B., Bruce, K., Beach, L. & Drago, A. 1992. Mechanistic Steps in the Production of PCDD and PCDF during Waste Combustion. Chemosphere, 25, pp. 1387-1392.

Gullett, B., Bruce, K. & Beach, L. 1992. Effect of Sulfur Dioxide on the Formation Mechanism of Polychlorinated Dibenzodioxin and Dibenzofuran in Municipal Waste Combustors. Environmental Science & Technology, 26, pp. 1938-1943.

Gullett, B., Lemieux, P. & Dunn, J. 1994. Role of Combustion and Sorbent Parameters in Prevention of Polychlorinated Dibenzo-p-dioxins and Dibenzofuran Formation during Waste Combustion. Environmental Science & Technology, 28, pp. 107-118.

Götaverken Miljö AB. 2013. Dioxin Removal by ADIOX®. Typical Applications in Various Flue Gas Cleaning Processes. [WWW]. [Cited: 31.1.2013]. Available at: http://www.gmab.se/documents/ENG_DioxinremovalbyADIOX_Typicalapplications_lq.pdf.

Hadzik, A. 2010. Role of DeNOx Catalyst in PCDD/F Emission Reduction in Hazardous Waste Incineration (HWI) Plant. Chemical and Biochemical Engineering, 24. pp. 401-408.

Hatanaka, T., Imagawa, T. & Takeuchi, M. 2003. Effects of Copper Chloride on Formation of Polychlorinated Dibenzo-p-dioxins in Model Waste Incineration. Chemosphere, 51, pp. 1041-1046.

Iino, F., Imagawa, T. & Gullett, B. 2000. Dechlorination-controlled Polychlorinated Dibenzofurans from Municipal Waste Incinerators. Environment Science & Technology, 34, pp. 3143-3147.

International Federation of Red Cross and Red Crescent Societies. 2002. [WWW]. [Cited: 18.12.2012]. Available at: http://www.ifrc.org/en/news-and-media/news-stories/asia-pacific/vietnam/vietnam-red-cross-urges-more-aid-for-agent-orange-casualties/

Janoschek, R. & Walter, M. 2003. Thermodynamic Properties of Chlorinated Phenols, Cyclo-C_5 Compounds, and Derived Radicals from G3MP2B3 Calculations. Journal of Molecular Structure, 661-662, pp. 635-645.

Kreisz, S., Hunsinger, H. & Vogg, H. 1996. Wet Scrubbers – A Potential PCDD/F Source? Chemosphere, 32, pp. 73-78.

Li, H.-W., Wang, L.-C., Chen, C.-C., Yang, X.-Y., Chang-Chien, G.-P. & Wu, E. 2011. Influence of Memory Effect Caused by Aged Bag Filters on the Stack PCDD/F Emissions. Journal of Hazardous Materials, 185, pp. 1148-1155.

Li X.-D., Zhang J., Yan J.-H., Chen T., Lu S.-Y. & Cen, K.-F. 2006. Effect of Water on Catalyzed De Novo Formation of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofurans. Journal of Hazardous Materials, A137, pp. 57-61.

Lomnicki, S. & Dellinger, B. 2002. Formation of PCDD/F from the Pyrolysis of 2-chlorophenol on the Surface of Dispersed Copper Oxide Particles. Proceedings of the Combustion Institute, 29, pp. 2463-2468.

Lundin, L. 2013. Umeå University, phone meeting.

Löthgren, C.-J. & Bavel, B. 2006. Dioxin Emissions after Installation of a Polishing Wet Scrubber in a Hazardous Waste Incineration Facility. Chemosphere, 61, pp. 405-412.

Metso Power Oy. 2012. Internal leaflet. Different fluidized bed boiler technologies.

Mroueh, U.-M., Tirkkonen, T., Laukkarinen, A., Hoffrén, H. 1988. Energiantuotannon päästöjen mittaaminen, PAH-, PCDD-, ja PCDF-yhdisteiden näytteenotto ja analytiikka. Valtion teknillinen tutkimuskeskus, Espoo, 1988. p. 60.

Mulholland, J. & Ryu J.-Y. 2001. Formation of Polychlorinated Dibenzo-p-dioxins by $CuCl_2$-catalyzed Condensation of 2,6-chlorinated Phenols. Combustion Science and Technology, 169, pp. 107-126.

Oksanen, A. 2004. Ilmansuojelu. Opintomoniste. Tampereen teknillinen yliopisto, Ympäristötekniikan osasto, Energia- ja prosessitekniikan laitos, Voimalaitos- ja polttotekniikka.

Olie, K., Vermeulen, P., Hutzinger, O. 1977. Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in The Netherlands. Chemosphere, 6, pp. 455-459.

Olie, K., Addink, R. & Schoonenboom, M. 1997. Metals as Catalysts during the Formation and Decomposition of Chlorinated Dioxins and Furans in Incineration Processes. Air & Waste Management Association, 48, pp. 101-105.

Qian, Y., Zheng, M., Liu, W., Ma, X. & Zhang, B. 2005. Influence of Metal Oxides on PCDD/Fs Formation from Pentachlorophenol. Chemosphere, 60, pp. 951-958.

Raghunathan K., Gullett B. 1996. Role of Sulfur in Reducing PCDD and PCDF Formation. Environment Science & Technology, 30, pp. 1827-1834.

Raiko, R., Saastamoinen, J., Hupa, M. & Kurki-Suonio, I. 2002. Poltto ja palaminen. 2. painos. Jyväskylä, Gummerus kirjapaino Oy. International Flame Research Foundation – Suomen kansallinen osasto. p. 750.

Ruokojärvi, P., Tuppurainen, K., Mueller, C., Kilpinen, P. & Ruuskanen, J. 2001. PCDD/F Reduction in Incinerator Flue Gas by Adding Urea to RDF Feedstock. Chemosphere, 43, pp. 199-205.

Ruokojärvi, P., Aatamila, M., Tuppurainen, K. & Ruuskanen, J. 2001. Effect of Urea on Fly Ash PCDD/F Concentrations in Different Particle Sizes. Chemosphere, 43, pp. 757-762.

Ryan, S., Li, X.-D., Gullett, B., Lee, C. & Touati, A. 2006. Experimental Study on the Effect of SO_2 on PCDD/F Emissions: Determination of the Importance of Gas-phase Versus Solid-phase Reactions in PCDD/F Formation. Environmental Science & Technology, 40, pp. 7040-7047.

Ryu, J.-Y. & Mulholland, J. 2002. Dioxin and Furan Formation on $CuCl_2$ from Chlorinated Phenols with One Ortho Chlorine. Proceedings of the Combustion Institute, 29 (2), pp. 2455-2461.

Ryu, J.-Y., Mulholland, J. & Chu, B. 2003. Chlorination of Dibenzofuran and Dibenzo-p-dioxin Vapor by Copper(II)Chloride. Chemosphere, 51, pp. 1031-1039.

Ryu, J.-Y., Mulholland, J., Dunn, J., Iino, F. & Gullett, B. 2004. Potential Role of Chlorination Pathways in PCDD/F Formation in Municipal Waste Incinerator. Environmental Science & Technology, 38, pp. 5112-5119.

Ryu, J.-Y., Mulholland, J., Takeuchi, M., Kim, D.-H. & Hatanaka, T. 2005. $CuCl_2$-catalyzed PCDD/F Formation and Congener Patterns from Phenols. Chemosphere, 61, pp. 1312-1326.

Ryu, J.-Y., Mulholland, J., Kim, D. & Takeuchi, M. 2005. Homologue and Isomer Patterns of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from Phenol Precursors: Comparison with Municipal Waste Incinerator Data. Environmental Science & Technology, 39, pp. 4398-4406.

Ryu, J.-Y., Choi, K.-C. & Mulholland, J. 2006. Polychlorinated Dibenzo-p-dioxin (PCDD) and Dibenzofuran (PCDF) Isomer Patterns from Municipal Waste Combustion: Formation Mechanism Fingerprints. Chemosphere, 65, pp. 1526-1536.

Samaras, P., Blumenstock, M., Lenoir, D., Schramm, K.-W. & Kettrup, A. 2000. PCDD/F Prevention by Novel Inhibitors: Addition of Inorganic S- and N-compounds in the Fuel before Combustion. Environmental Science & Technology, 34, pp. 5092-5096.

Shaub, W., Tsang, W. 1983. Dioxin Formation in Incinerators. Chemosphere, 17, pp. 721-730.

Simatek A/S. 2012. Simatek “Dry Flue Gas Cleaning Concept”. Brochure. [PDF]. [Cited: 23.1.2013]. Available at: http://www.simatek.dk/documents/00006.pdf

Sommeling, P., Mulder, P., Louw, R. 1994. Formation of PCDFs during Chlorination and Oxidation of Chlorobenzenes in Chlorine/Oxygen Mixtures of Around 340 ºC. Chemosphere, 29. pp. 2015-2018.

Stieglitz, L., Zwick, G., Beck, J., Roth, W., Vogg, H. 1989. On The De-novo Synthesis of PCDD/PCDF on Fly Ash of Municipal Waste Incinerators. Chemosphere, 18, pp. 1219-1226.

Sun, R.-D., Irie, H., Nishikawa, T., Nakajima, A., Watanabe, T. & Hashimoto, K. 2003. Suppressing Effect of CaCO3 on the Dioxins Emission from Poly(vinyl chloride) (PVC) Incineration. Polymer Degradation and Stability, 79, pp. 253-256.

Suzuki, K., Kasai, E., Aono, T., Yamazaki, H. & Kawamoto, K. 2004. De Novo Formation Characteristics of Dioxins in the Dry Zone of an Iron Ore Sintering Bed. Chemosphere, 54, pp. 97-104.

Takaoka, M., Shiono, A., Nishimura, K., Yamamoto, T., Uruga, T. & Takeda, N. 2005a. Dynamic Change of Copper in Fly Ash during De Novo Synthesis of Dioxins. Environmental Science & Technology, 39, pp. 5878-5884.

Takaoka, M., Yamamoto, T., Shiono, A., Takeda, N., Oshita, K. & Matsumoto, T. 2005b. The Effect of Copper Speciation on the Formation of Chlorinated Aromatics on Real Municipal Solid Waste Incinerator Fly Ash. Chemosphere, 59, pp. 1497-1505.

Takaoka, M., Fujimori, T., Oshita, K., Shiota, K., Tanida, H. & Morisawa, S. 2008. Determination of Catalytic Reactions with Copper during Dioxin Formation. Organohalogen compounds, 70. p. 4.

Tame, N., Dlugogorski, B. & Kennedy, E. 2007. Formation of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans (PCDD/F) in Fires of Arsenic-free Treated Wood: Role of Organic Preservatives. Environmental Science & Technology, 41, pp. 6425-32.

Tang, H. 2003. The Shell Dioxin Destruction System. The Royal Dutch Shell Group (CRI International). Solid & Hazardous Waste Management Conference, Singapore. p. 10.

Tuppurainen, K., Halonen, I., Ruokojärvi, P., Tarhanen, J. & Ruuskanen J. 1998. Formation of PCDDs and PCDFs in Municipal Waste Incineration and its Inhibition Mechanisms: A Review. Chemosphere, 36, pp. 1493-1511.

United States Environmental Protection Agency. 1987. Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and Dibenzofurans (CDDs and CDFs). Risk Assessment Forum, 57 p.

Wiater, I., Born, J. & Louw, R. 2000. Products, Rates and Mechanism of the Gas-Phase Condensation of Phenoxy Radicals Between 500-840 K. European Journal of Organic Chemistry, 6, pp. 921-928. Cited: Altarawneh M. et. al 2009.

Wang, L.-C., Hsi, H.-C., Chang, J.-E., Yang, X.-Y., Chang-Chien, G.-P., Lee, W.-S. 2007. Influence of Start-Up on PCDD/F Emission of Incinerators. Chemosphere, 67, pp. 1346-1353.

Waste Control. 2013. Database of Waste Management Technologies. [WWW]. [Cited: 29.5.2013]. Available at: http://www.epem.gr/waste-c-control/database/html/WtE-00.htm

Weber, R. & Hagenmaier, H. 1999a. Mechanism of the Formation of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from Chlorophenols in Gas Phase Reactions. Chemosphere, 28, pp. 529-549.

Weber, R. & Hagenmaier, H. 1999b. PCDD/PCDF Formation in Fluidized Bed Incineration. Chemosphere, 38, no. 11, pp. 2643-2654.

Weber, R., Takasuga, T., Nagai, K., Shiraishi, H., Sakurai, T., Matuda, T. & Hiraoka, M. 2002. Dechlorination and Destruction of PCDD, PCDF and PCB on Selected Fly Ash from Municipal Waste Incineration. Chemosphere, 46, pp. 1255-1262.

Wikström, E. & Marklund, S. 2000. Secondary Formation of Chlorinated Dibenzo-p-dioxins, Dibenzofurans, Biphenyls, Benzenes and Phenols during MSW Combustion. Environmental Science & Technology, 34, pp. 604-609.

Wikström, E., Ryan, S., Touati, A., Tefler, M., Tabor, D. & Gullett, B. 2003a. Importance of Chlorine Speciation on De Novo Formation of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans. Environmental Science & Technology, 37, pp. 1108-1113.

Wikström, E., Ryan, S., Abderrahmane, T. & Gullett, B. 2003b. Key Parameters for De Novo Formation of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans. Environmental Science & Technology, 37, pp. 1962-1970.

World Health Organization. 2000. Chapter 5.11 Polychlorinated dibenzodioxins and dibenzofurans. [PDF]. [Cited: 24.1.2013]. Available at: http://www.euro.who.int/__data/assets/pdf_file/0017/123065/AQG2ndEd_5_11PCDDPCDF.pdf

Xie, W., Liu, K., Pan, W.-P. & Riley, J. 1999. Interaction between Emissions of SO_2 and HCl in Fluidized Bed Combustors. Fuel, 78, pp. 1425-1436.

Yamamoto, T., Inoue, S. & Sawachi, M. 1989. Post Furnace Formation and Progressive Chlorination of PCDD and PCDF in Municipal Waste Incinerator. Chemosphere, 19, pp. 271-276.

Yan, J.-H., Chen, T., Li, X.-D., Zhang, J., Lu, S., Ni, M. & Cen, K. 2006. Evaluation of PCDD/F Emissions from Fluidized Bed Incinerators Co-firing MSW with Coal in China. Journal of Hazardous Materials, A135, pp 47-51.

Zumdahl S. 2005. Chemical Principles: Fifth Edition. Boston, USA. Houghton Mifflin Company, p. 1070 + 94 (append.).

D 2010/75/EU. Directive of the European Parliament and of the Council of 24 November 2010 on Industrial Emissions (integrated pollution prevention and control). [PDF]. [Cited: 24.2.2013]. Available at: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2010:334:0017:0119:en:PDF

S/EN1948-1/2006. European Standard EN 1948-1. Stationary Source Emissions – Determination of the Mass Concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 1: Sampling of PCDDs/PCDFs. Approved by European Committee for Standardization on 23 January 2006. p. 62